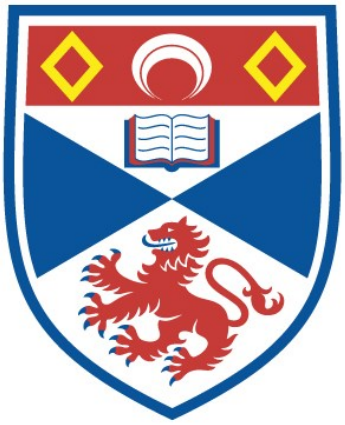
THE DEVELOPMENT OF A QUINQUAQUADRUPOLE MASS SPECTROMETER : THE STUDY OF ION-MOLECULE REACTIONS IN THE GAS PHASE USING MULTIPLE QUADRUPOLE INSTRUMENTS

Robin Gibson Hall

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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THE DEVELOPMENT OF A QUINQUAQUADRUPOLE MASS SPECTROMETER- THE STUDY OF ION-MOLECULE REACTIONS IN THE GAS PHASE USING MULTIPLE QUADRUPOLE INSTRUMENTS.

A thesis presented by

Robin Gibson Hall, B.Sc.(Hons)

to the University of St. Andrews
in application for the Degree of Doctor of Philosophy.

Date: August 1990.

DECLARATION

I, Robin Gibson Hall, hereby certify that this thesis has been composed by myself, that it is a record of my own work, and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

.....

Robin Gibson Hall

10th July 1990.

CERTIFICATE.

I hereby certify that Robin Gibson Hall B.Sc., has spent twelve terms at research work under my supervision, has fulfilled the conditions of the Resolution of the University Court, 1967, No1 and is qualified to submit the accompanying thesis in application for the Degree of Doctor of Philosophy.

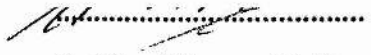
.....

Dr J . C Walton.

Director of Research

10th July.1990

I was admitted to the Faculty of Science of the University of St Andrews under Ordinance General No. 12 on 1st October 1987.



Robin Gibson Hall

10th July 1990.

POSTGRADUATE LECTURES ATTENDED.

During my Postgraduate Research I have fulfilled the Postgraduate Lecture requirements by attending the following courses:-

1. Introductory German Course.
2. Intermediate German Course.
3. Case Studies in Mechanistic Chemistry.
4. Chemical Carcinogenesis.
5. Some aspects of Inorganic Phosphorus Chemistry.
6. Crystal Structure Determination.
7. Use of the Apple Macintosh Word Processor.
8. Radical Clocks.
9. Semi-Conductor Growth Technology.

Robin Gibson Hall.

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To Jennifer,
thanks for being around when it
mattered most.

Contents.

Abstract.

The field of quadrupole mass spectrometry has grown enormously since the early 1980's. The invention of the triple quadrupole mass spectrometer led to the development of tandem quadrupole mass spectrometers of many different configurations. A large number of tandem quadrupole mass spectrometers have also been developed by linking one or more quadrupole mass filters to a traditional magnetic or electric filter.

The versatility of multiple quadrupole mass spectrometers along with their potential to rapidly produce a huge amount of data on a particular ion makes them ideal instruments for routine analytical analysis as well as for fundamental research

The quinquaquadrupole mass spectrometer has been developed as an extension to the available multiple quadrupole systems. It offers the possibility to obtain even more data on the fragmentation of ions as well as enabling the study of novel ions to be carried out.

The development of the quinquaquadrupole mass spectrometer forms the main part of this thesis. Also discussed are the reactions studied to evaluate the instrumental performance.

The the ion molecule reactions of some halogen containing cations with saturated and unsaturated hydrocarbons performed on the triple quadrupole mass spectrometer are also discussed

Chapter one.

Literature review of the development of tandem mass spectrometry and its applications. A detailed account of the development of tandem quadrupole mass spectrometers is presented.

1.Introduction.

This review will cover three distinct areas of mass spectrometry. A brief summary tracing the early development of mass spectrometry up to the introduction of tandem mass spectrometers will be given. This will be followed by an examination of the development of tandem mass spectrometers up to the introduction of the quadrupole mass filter. Finally an account will be given of the development of multiquadrupole instruments, The development of the triple quadrupole mass spectrometer and its applications will be examined in detail. Current developments in instrumentation including the quadrupole ion trap and ion trap quadrupole combination instruments will also be described. .

1.10. Mass spectrometry.

The first mass spectrograph was published in 1901[1]. Positive ions from a discharge tube were focussed and then passed into the mass analyser where they were separated by the combined effects of the magnetic and electric field. Ions were detected on a fluorescent screen. An improved instrument with a much enhanced resolution[2] was soon developed. Positive ions were generated in a discharge tube, focussed by means of two slits and then detected first

by an electric field and then by a magnetic field. Ions of different m/e ratios followed different paths and reached the photographic plate at different points giving a mass spectrum of parallel lines. This instrument was used to investigate the isotopes of different elements. A further instrumental development was reported around the same time[3]. Ions of different m/e ratios were deflected through different radii through a slit to a detector. Although improvements to the instrumental resolution were achieved as a result of these improvements in instrumentation, further enhancement of the resolution was required to study lighter elements. A mass spectrometer capable of high mass discrimination of and a resolution of 2000 was developed by enlargement of the analyser and making the focussing slits narrower[4].

One of the most significant developements in the early design of mass spectrometers was the introduction of the sector magnetic analyser[5]. The ions of differing masses were deflected to differing extents by a wedge shaped magnetic field. There was a great deal of activity in the developement of magnetic sector analysers of 180^{o}, 90^{o}[6] and 60^{o}[7] configurations. The sector instrument had the advantage over previous mass spectrometers that the source and detector were free from the mass descriminating influence of the analyser field.

1.11 Double focussing mass spectrometers

The concept of multi-stage double focussing mass spectrometers was first reported by Mattauch and Hertzog.[8] A schematic representation of their original instrument is shown in figure 1.1. Ions are detected as a series of bands on a photographic plate. The density of each band is measured and this is a measure of the number of ions of a particular mass present. The use of a photographic plate for ion detection is rather slow as each plate has to be developed. However an advantage of the method is that all ions are recorded simultaneously and so fluctuations in the ion abundances during a scan do not affect the overall results.

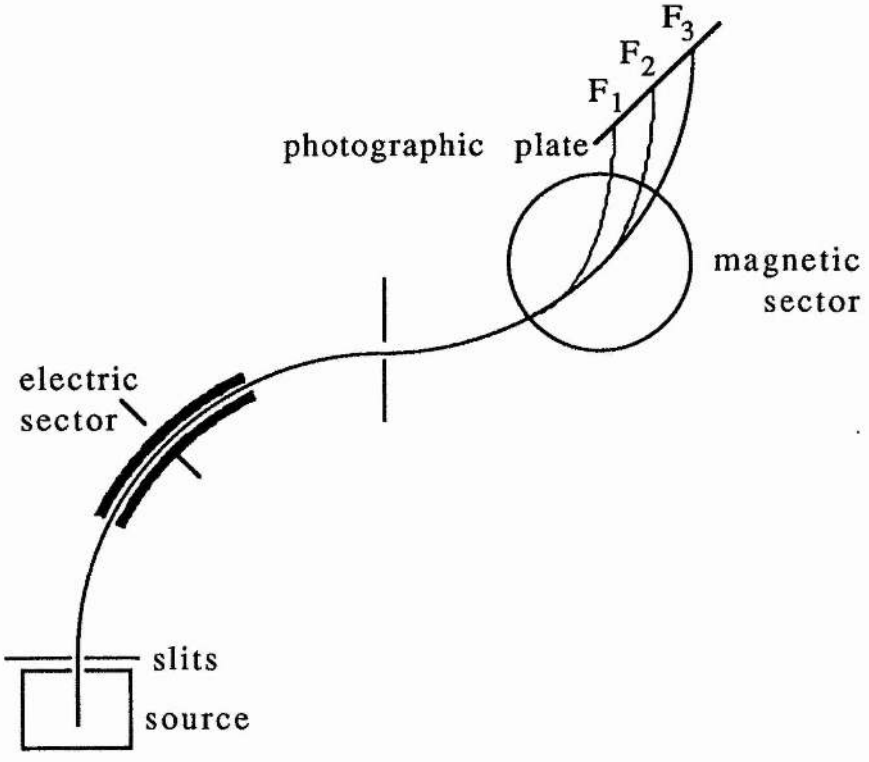


Figure1.1 The Mattauch Hertzog instrument.

There was a rapid growth in this field with a number of groups developing instruments of different configurations. Barber[9] demonstrated that the decompositions of metastable ions formed in the field-free region between the magnetic and electric sectors of the instrument could be followed.

An ion of a particular mass could be selected and passed into the field free region of the instrument. The voltages on the plates could be reduced to allow daughter ions of lower kinetic energy to pass to the detector. This technique had great advantages over its predecessors in that the mass range over which daughter ions could be monitored was essentially unlimited. There were however disadvantages, particularly that ions of all energies were passed by the electric sector giving a spectrum of very broad peaks making interpretation difficult. The problems were overcome by the development of a technique known as linked scanning mass spectrometry[10]. This involves the simultaneous increasing of the acceleration voltage and electric sector field keeping E^2/V constant, thus enabling all ions to be focussed and giving a spectrum of sharp peaks. Other linked scanning instruments were developed, these allowed increase in the available mass range of the instrument[11]. Linked scanning modes have recently been described for all combinations of electric, magnetic and quadrupole hybrids[12]

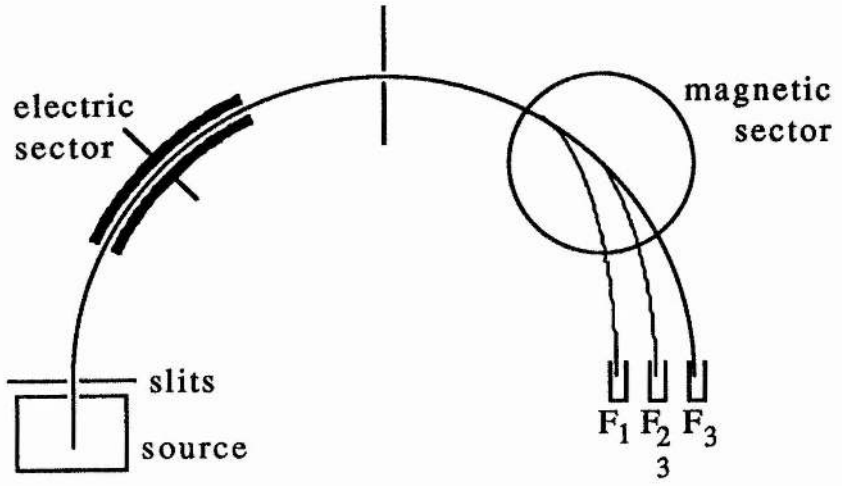


Figure1.2. Double focussing mass spectrometer of Nier-Johnson geometry.

Figure 1.2 shows a schematic diagram of a double focussing mass spectrometer of Nier-Johnson geometry [13]. The ions are accelerated away from the ion source, and the beam then passes into the electric sector of the instrument. A potential across the metal plates focuses the beam at a slit. The ion beam then passes through a magnetic field where ions of differing m/e values are separated. Ions of different mass have different radii of curvature. The ions are detected by varying the magnetic field strength and therefore bringing each different mass to the same focus point. The double focussing instrument is capable of high resolution and very accurate mass measurement.

1.12 Reverse geometry double focussing mass spectrometers.

Mass spectrometers having a magnetic sector followed by an electric sector are referred to as reverse geometry

instruments[14]. The study of metastable ion decomposition using double focussing mass spectrometer was considerably improved when Benyon[15] developed a reverse geometry instrument. Instruments of this type are useful for the study of metastable ions. The magnetic sector of the instrument can be set to select an ion of particular mass. This ion may then pass into the field free region of the instrument where it may undergo decomposition giving metastable ions. The ions formed may then be separated by scanning the the electric sector according to the differing kinetic energies. This technique is known as M.I.K.E.S (Mass Analysed Ion Kinetic Energy Spectroscopy)[16].This technique is used for the identification of structural differences within large molecules. It has been used to identify compounds present in complex mixtures [17]. This is done by selecting the molecular ion of the compound of interest and observing the ions formed during decomposition. The technique is extremely fast and sensitive. It does however suffer from certain disadvantages in that the spectra produced are often very complicated and require a considerable amount of interpretation.

1.13 Triple focussing mass spectrometers.

Another problem encountered when analysing mixtures of compounds using reverse double focussing mass spectrometer is the inability of the instrument to separate ions of the same mass. This is because the ions are not

energy focussed before passing into the magnetic sector. A triple focussing mass spectrometer overcomes this problem by the introduction of a second electric sector between the ion source and the magnetic source[18]. This is shown in figure 1.3.

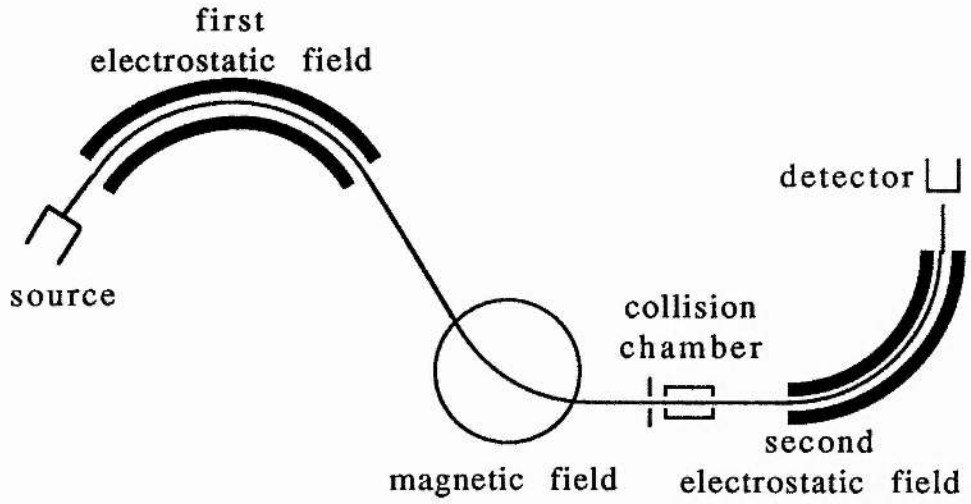


Figure1.3 Triple focussing mass spectrometer of EBE configuration

1.2 Tandem mass spectrometry.

Conventional mass spectrometers provide a rapid means of structural analysis, however the data produced are insufficient to give unambiguous compound identification on

their own and are inadequate for direct analysis of samples containing more than one component. The coupling of a gas chromatograph with a mass spectrometer (GC/MS) produced one of the most successful and widely used analytical instruments to date[19]. Tandem mass spectrometry evolved as a result of the success of the GC/MS instrumentation, and has been shown to be a rapid method by which the analysis of complicated mixtures of compounds can be rapidly carried out.. Early tandem instruments were designed for the analysis of complex mixtures. Components of a mixture of toluene, styrene, phenol, benzene and ethyl-benzene were identified. [20] The molecular ion of each component could be selected and passed into the field free region between the two mass analysers. Collisional dissociation of the ion would occur and the resulting daughter ions could be mass separated by the second mass spectrometer and recorded. Tandem instruments have also been used for characterization of isomeric ions[21] and for the analysis of pyrolysis products of DNA.[22] Tandem mass spectrometers similar in design to figure1.4.

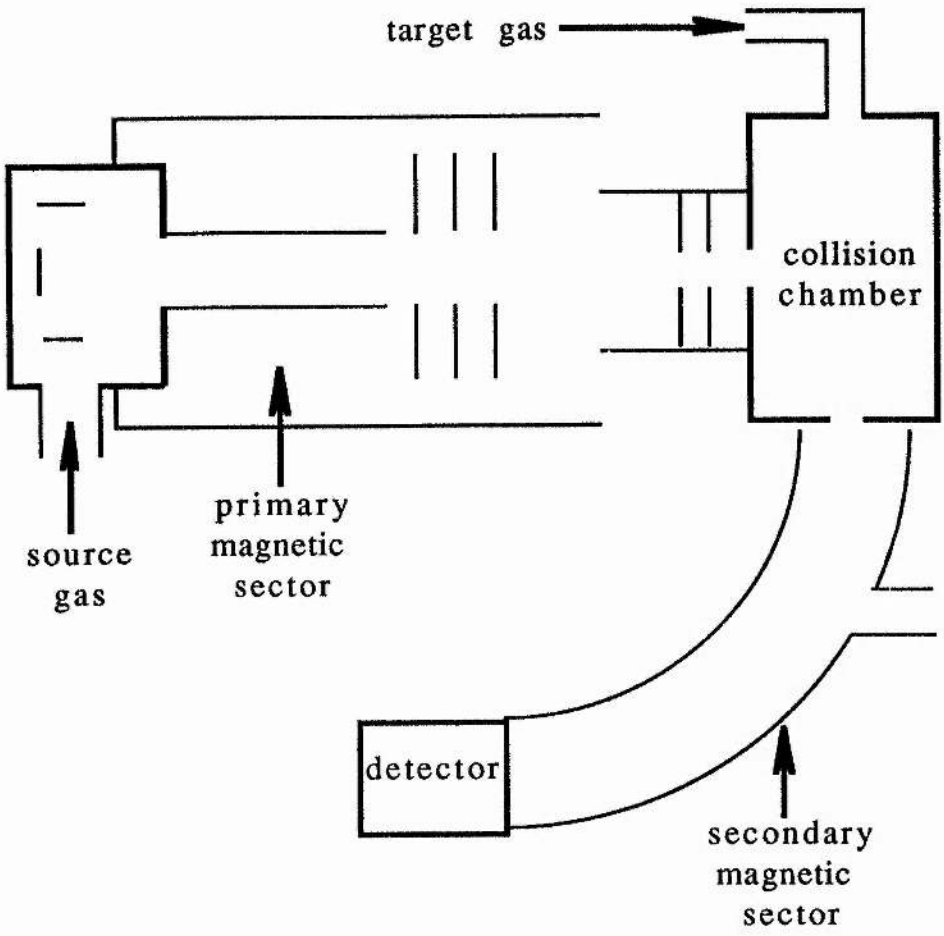


Figure1.4. Typical tandem mass spectrometer..

have been successfully employed for charge exchange studies[23,24,25] By the introduction of a target gas into the collision chamber ion-molecule reactions may be studied. The instrument shown above is less suited to the study of ion-molecule reactions involving collision of the primary ion with the neutral target because the momentum imparted on the product ions would take them out of the catchment area of the magnetic sector of the instrument..

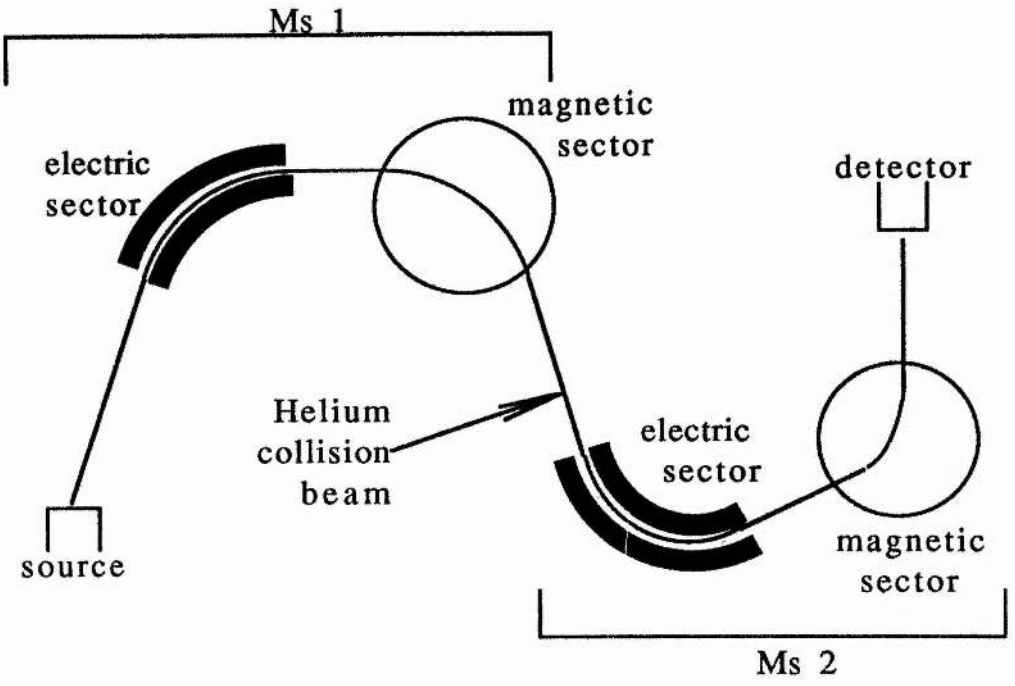


Figure1.5. Tandem mass spectrometer employing two double focussing mass spectrometers.

Figure1.5 represents the first tandem instrument to employ two double focussing mass spectrometers.[26] This instrument made high resolution of both the parent and daughter ions possible. However it had the disadvantage of being large and also very expensive to construct.

1.20 Hybrid Quadrupole (Q) / Magnetic (B) / Electric (E) Sector Instruments.

The use of a quadrupole as the first mass analyser in a tandem instrument limits the mass range available and the resolution. To overcome this an instrument with a magnetic

sector preceding a quadrupole collision cell and a quadrupole mass filter as the mass analyser(B.Q.Q) was developed. [27] The instrument could also be adapted to give a quadrupole mass filter followed by a quadrupole collision cell and a magnetic sector analyser(Q.Q.B) configuration[28].

An instrument of (E.Q) geometry has been constructed to study ion dissociation pathways[29]. It has the advantage over the (B.E.Q) type instrument of being both small and inexpensive to construct. However there is a considerible loss in resolving power through the removal of the magnetic sector of the instrumnet.

An instrument of B.E.E.B. geometry has been constructed [30] for structural studies of ions. Metastable ions are formed in the field free region before the first magnetic sector and passed through to a collison cell between the first magnetic and electric sectors were a collision with a neutral gas occurs producing fragment ions. A particular fragment ion is selected and passed through to the third field free region between the third and the fourth sectors. The ion is collisionally dissociated and the fragments are detected by linked scanning of the third and fourth sectors. The instrument has been used for sequencing studies of small peptides.

A further improvement on the existing tandem mass spectrometers was the introduction of an instrument incorporating a double focussing mass spectrometer as the first stage of the instrument, followed by two sets of

quadrupole rods giving an instrument of (BEQQ) geometry figure 1.6.[31]

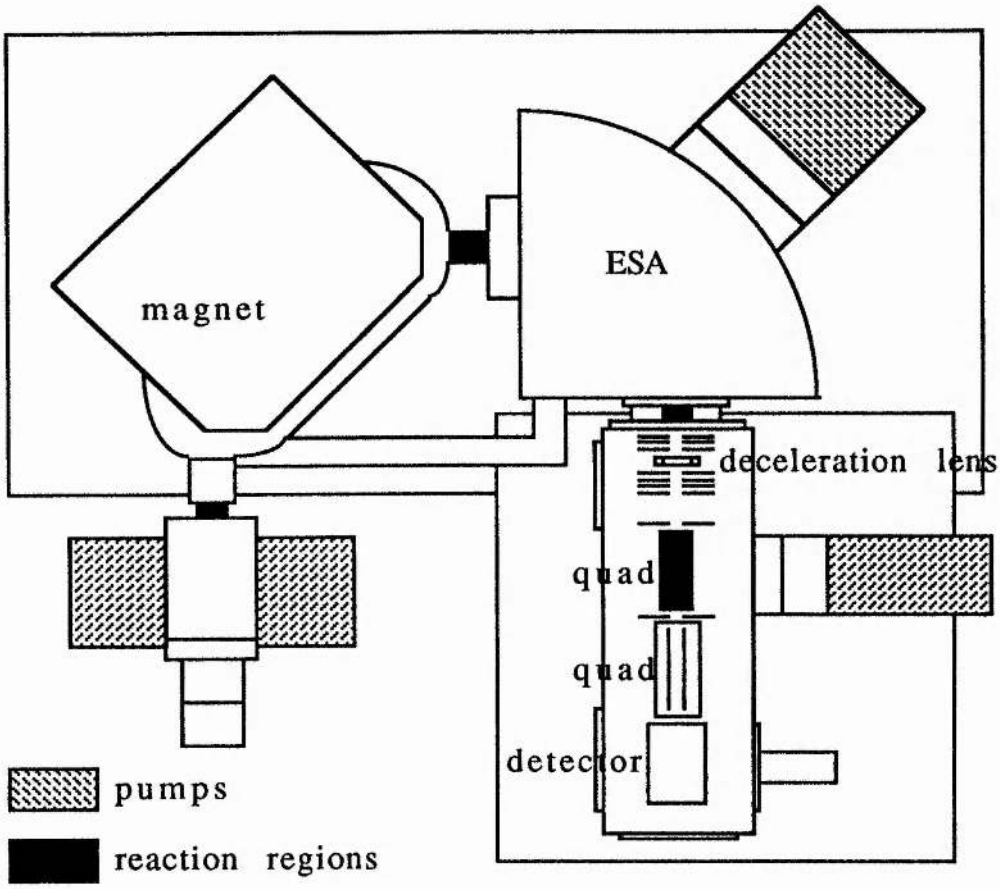


Figure 1.6. Schematic diagram of a hybrid BEQQ mass spectrometer.

As with all hybrid instruments involving the passage of ions from an electric sector to a quadrupole unit the major difficulty in the developement of this instrument was the deceleration of the ions before they entered the the quadrupole. The was achieved using a lens system between the electric and the quadrupole sectors. The quadrupoles

were also mounted on a rail system to enable their alignment to be altered easily.

This instrument allowed both the fragmentation studies at high kinetic energies normally performed on magnetic/ electric sector instruments and the low kinetic energy studies characteristic of the quadrupole instruments. A more recent BEQQ spectrometer has been developed and used to study the ion-molecule reactions of CH_3CHOH^+ and $CH_3OCH_2^+$ with vinyl methyl ether[32]. The instrument has also been used to distingiush between $C_4H_9O^+$ isomers by their collisionally induced dissociation patterns[33].

An instrument of EBQQ geometry has also been reported[34]. This type of instrument has been used to separate and analyse a mixture of dimethylaniline (m/e121.08915) and methyl anisole (m/e121.06534) demonstrating its high resolving power.

Further combinations of electric, magnetic and quadrupole sectors have been reported[35,36]. The combinations so far discussed offered either high resolution of parent ion followed by moderate resolution of daughter ions or visa-versa. .

A tandem quadrupole fourier transform mass spectrometer has been reported[37]. In this system ion production is separated from the ion analysis. A double quadrupole system is used to first separate out the ion of interest and the second serves to guide the ion into the magnetic sector of the instrument.

1.3 Quadrupole mass spectrometry.

1.30 General introduction

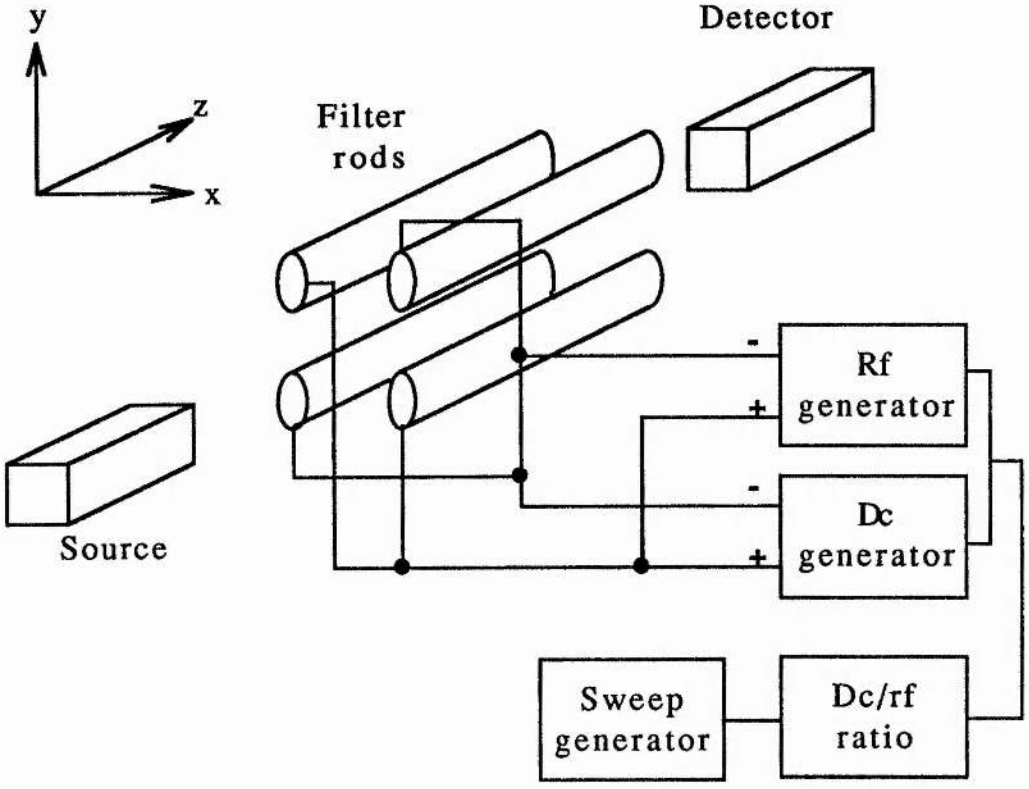


Figure1.7. Electrical connections to a set of quadrupole rods.

A quadrupole consists of four accurately machined and aligned electrically conducting rods arranged as shown in figure 1.7. The rods are usually made from stainless steel, and are generally housed in precision ground ceramics. Ideally the rods should all be hyperbolic in shape. However for ease of manufacture cylindrical rods are used in most of

today's commercial instruments[38]. If the radius of the rods is R and r_o is half the distance between opposite pairs of electrodes of the quadrupole then to achieve a good approximation to the ideal quadrupole field

$$R = 1.1487 r_o$$

The field within the analyser is created by coupling opposite pairs of rods together and applying an electrostatic potential between each pair. In addition opposite pairs of rods are biased with dc potentials positively or negatively with respect to the potential on the axis of the array of rods.

An ion entering the rod system at one end will move parallel to the z axis. The combination of applied rf and dc fields will cause the ion to undergo transverse motion. The ion may oscillate about the z axis and pass through the quadrupole system or move away from the z axis and strike a rod. By selecting the correct parameters an ion of a particular mass can have a stable trajectory and pass through the quadrupole system while all other ions will have unstable trajectories and will strike the rods. High sensitivities are achieved by the use of large rod diameters and long rods. The larger the rod diameter and the longer its length the higher are the required voltages. Today's commercial instruments employ typical rod diameter of between 6 and 8mm and typical rod lengths of 125 to 140mm. A huge number of mass spectrometers incorporating a quadrupole section have been developed.[39].

A dual source quadrupole mass spectrometer allowing the detection of both ions and their neutral fragments was developed by Reeher [40] Utilizing the fact that a quadrupole makes no discrimination between positive and negative ions a mass spectrometer capable of analysing for both has also been reported.[41] The ions are deflected to two separate multipliers and detected separately.

The motion and transmission of ions in a quadrupole field are dependent on the variation of the applied potentials with time and require complex mathematical modelling to predict them. A detailed treatment of the mathematics can be found in a number of textbooks and reviews[42,43]. Only a simplified treatment of the physics of ion motion in a quadrupole field will be considered here.

The equations relating ion motion to the applied potentials and the physical constraints of the quadrupole system are known as the Mathieu equations. The general form of this equation is ...

$$\frac{d^2x}{dy^2} + (a + 2q\cos wt)x = 0$$

Where:

x= The displacement of the ion from the z axis.

y= The time function.

a= $8eU/Mr_o^2w^2$

q= $4eV/Mr_o^2w^2$

Two solutions exist to the Mathieu equations the first, where both x and y continue to increase with time, gives non bounded and therefore unstable ion flight paths. The second, where x or y is periodic with time, gives stable flight paths providing the distance the ion travels from the z axis is not greater than the inner radius r_o of the quadrupole rods. The values of **a** and **q** which give stable or unstable flight paths are located in distinct areas of a graph of **a** verses **q**. A plot of this type is shown in figure 1.8.

For an ion to be transmitted by a quadrupole mass filter the values of **a** and **q** must lie within area w, any values lying outside this region giving unstable flight paths.

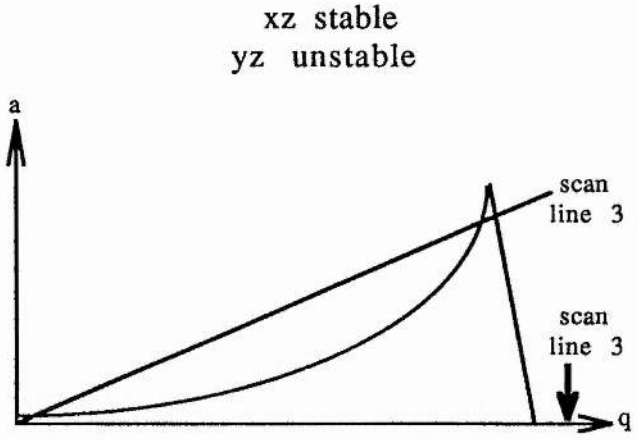


Figure 1.8. An a/q stability plot for a quadrupole mass filter

If the mass filter is switched from rf/dc mode to rf only the scan line follows the x axis. The spectrum obtained when operating in this mode is shown in figure 1.9

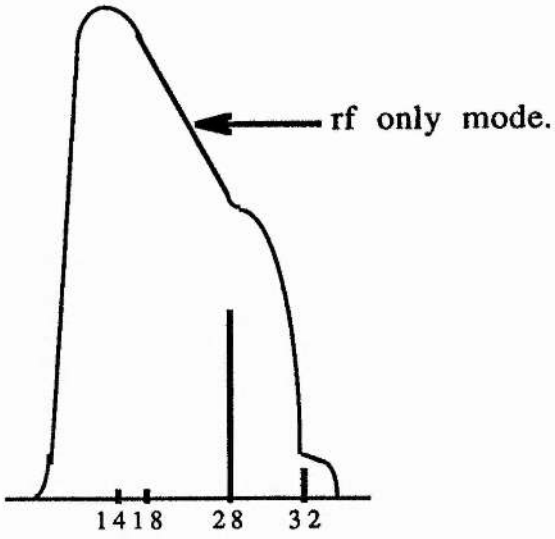


Figure 1.9 Operation of the quadrupole mass spectrometer in the rf only mode (scan line 2).

In this case all ions are transmitted. As the scan passes through the stability boundary for an ion it is rejected. This corresponds to the steps in the mass spectrum. The rf only mode of operation does have a use in the detection of peaks at high mass which may not be within the instrumental mass range. Groups of fragment ions, too weak to be detected individually may also be observed when using the instrument in this mode.

1.31 Resolution of ions in a quadrupole mass filter.

A set of quadrupole rods will resolve ions well only if the electrostatic field within the analyser is uniform. Deviations from uniformity arise due to the use of the cylindrical rods rather than the hyperbolic. It has been noted that the

resolution is enhanced by a factor of between two and three if the rods are made hypobolic[44]. Non-uniformity also gives rise to poor resolution and peak splitting in the spectrum[45]. Another major factor which influences the ability of the quadrupole mass filter to resolve is the requirement of a constant rf/dc ratio to be maintained throughout the mass scan. The ratio must not vary more than 1 part in10^5(see reference 46).

The quadrupole mass analyser.

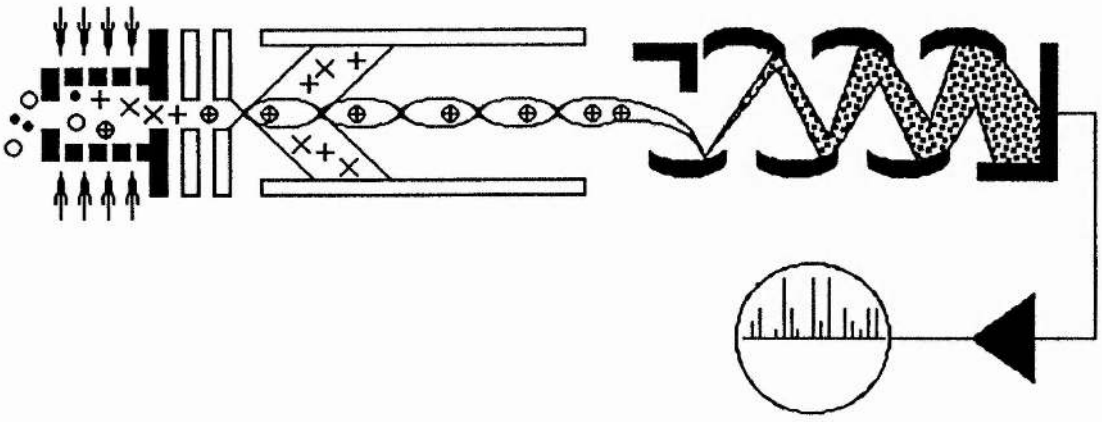


Fig 1.10 The Quadrupole Mass Analyser.

A quadrupole mass analyser separates ions on the basis of their mass to charge ratio.

1.32 The monopole mass filter.

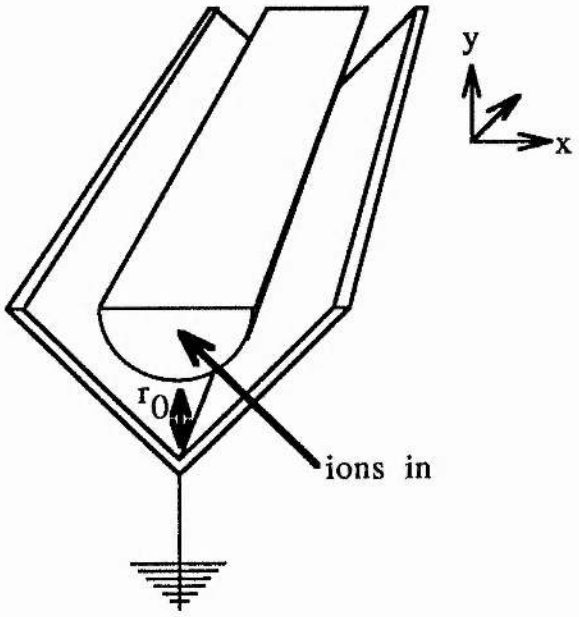


Figure 1.11 Schematic representation of the monopole.

The monopole mass filter was first reported by Von Zahn[47]. A schematic representation is shown in figure1.11. It is made from two electrodes, one is circular and the other is shaped as a right angle. By superimposing rf and dc voltages a quarter of a quadrupole field is set up. The monopole has the advantage of low cost and simplicity over the quadrupole, however it has not become an important commercial instrument.

1.4 Tandem quadrupole mass spectrometers.

The preceding section explained the mode of operation of the quadrupole mass filter. This type of mass filter has unique advantages over conventional magnetic or electrical analysers in that ion selection is not velocity dependent. Quadrupole mass filters therefore have specific benefits when used in the construction of tandem mass spectrometers.

An early tandem quadrupole mass spectrometer[48] consisted two quadrupole mass filters. An ion of interest could be separated by the first quadrupole and passed into a collision chamber. The second quadrupole could be used in a linear configuration or could be turned through 90^0 to detect scattered ions. Double quadrupole systems have also proved useful for the rapid analysis of trace components in complex mixtures[49]. Figure1.12 illustrates the use of two quadrupole mass analysers operating as a Sector Analyser Mass Spectrometer(S.A.M.S)[50]. The first quadrupole operates as a notch filter to remove unwanted ions and the second operates as a conventional mass filter.

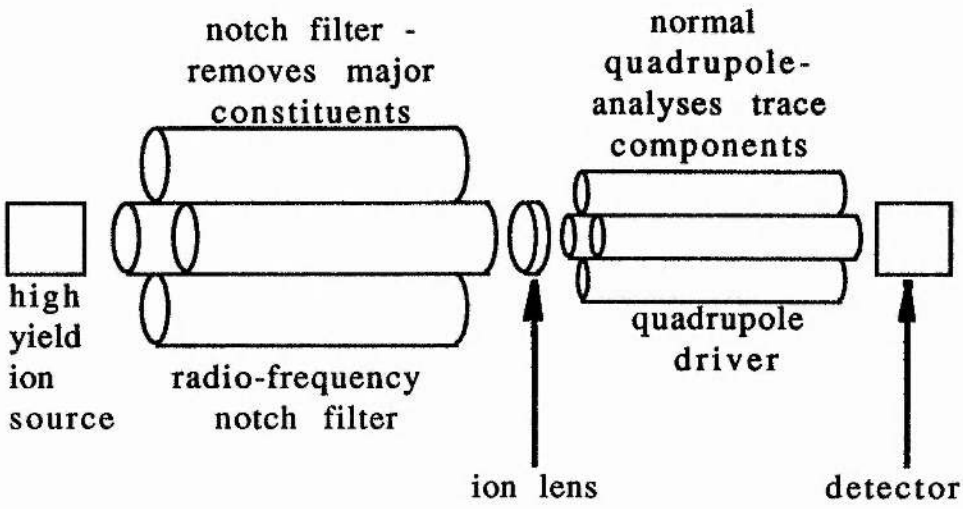


Figure1.12. The double quadrupole notch filter system.

The first quadrupole acts as a separation device and the second acts as an analyser. Between the two is a collision region where ions undergo collision induced dissociation. An instrument of this type has been constructed and used for complex mixture analysis[51]. The introduction of a collision cell between the two quadrupoles allowing the introduction of a collision gas was reported by Cookes [52].

The introduction of a quadrupole as a collision cell increased the degree of ion focussing possible and reduced the scattering, thus helping the detection of minor daughter ions. A double quadrupole instrument was developed by Siegel [53] which behaved in a similar manner to the triple quadrupole mass spectrometer. Instead of using a second rf- only quadrupole as a collision chamber the instrument employed the dielectric properties of ferrite tubing as the

collision chamber. A diagram of the apparatus is shown in Figure 1.13.

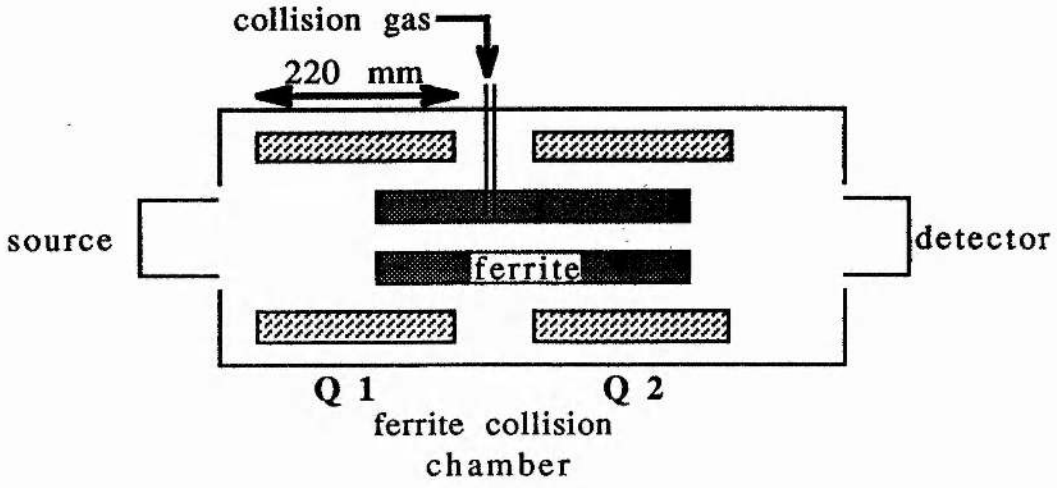


Figure1.13 Double quadrupole system with ferrite chamber.

Its advantages over the triple quadrupole mass spectrometer were cost and size reduction and simplicity of electronics. The ferrite focussing effect greatly improved the transmission of ions. (See Chapter 4 Section 4.61 for detailed description of ferrite usage in Quadrupole Mass Spectrometry). This led to the development of the triple quadrupole mass spectrometer designed by Morrison and McGilvary[54] and Vestal and Futrell decribed in 1979 [55]. The original triple quadrupole mass spectrometers were designed to study the photodissociation of ions. A primary ion could be selected by operation of the first quadrupole as a mass filter and passed into the second quadrupole. Irradiation of the selected ion by either passing a laser beam along the axis of the quadrupoles or passing a beam from a mercury lamp through the second quadrupole yielded the secondary fragments. These were mass

analysed by operation of the third quadrupole as a mass filter. These early triple quadrupoles suffered from secondary ion production by collision induced dissociation which interfered with the photodissociation spectra. Modification of this apparatus to allow the introduction of a collision gas into the second quadrupole was achieved by Yost and Enke[56]. A schematic diagram of the apparatus is shown in figure2.1. The instrument was used for the study of collisionally induced dissociation of parent ions[57] as the confinment of ions in the second chamber gave high fragmentation efficiency at lower ion kinetic energies than had previously been possible(5-20eV). The versatility of the instrument was shown by its use in mixture analysis [58] and structure elucidation[59]. The triple quadrupole mass spectrometer has been used for sequential collisionaly induced dissociation studies[60]. Over 400 fragmentation pathways have been determined for the fragmentation of nonan-4-one. This work illustrates the potential of a triple quadrupole system linked to a computer library of standardised CID dissociation patterns for structural elucidation. Minor modifications to the detector potentials allowed studies to be made of negative ions produced in CID processes[61]. Hunt constructed a triple quadrupole mass spectrometer similar to the original to study the collisionally induced dissociation of negative ions and carbanion reactions in the gas phase [62]. More recently a triple quadrupole mass spectrometer has been employed in the study of the reactivity of $CH_3OCH_2^+$ and CH_3CHOH^+

isomers[63]. The studies show marked differences in the CID fragmentation patterns resulting from the collision with nitrogen in the second quadrupole. Collisionally induced dissociation studies using a triple quadrupole mass spectrometer have also been shown to have useful biochemical applications[64].The CID spectra of permethylated D(-)-ribose and D(-)-arabinose isomers have been used to distinguish between the two compounds.

The triple quadrupole has the advantage in MS-MS studies of unit resolution at low to medium molecular weight and discrimination of ions on their m/e ratio alone. Dawson describes the triple quadrupole mass spectrometer as 'a complete on line synthetic laboratory.[65] and illustrates the versatility of the instrument by generating and studying the reactions of protonated esters with ammonia in the the second quadrupole. However it is clear from this study that accurate control of the axial kinetic energy of the reactant ion and the thickness of the target gas are important perameters in the study of ion molecule reactions using a triple quadrupole instrument.

The triple quadrupole mass spectrometer can be switched rapidly to different modes of operation producing a large amount of detailed structural information [66]. A normal mass spectrum of a sample may be obtained by operating the first quadrupole as a mass filter and the second and third quadrupoles in rf- only mode with no collision gas in the second chamber. Structural information on a sample may be obtained by selecting an ion in the first quadrupole

and passing it into a neutral collision gas in the second. A mass spectrum of the resulting fragments can be obtained by operating the third quadrupole as a mass filter. Ion molecule reactions may be investigated by the selection of a fragment ion in the first quadrupole and the introduction of a target gas into the second, operating in the rf only mode. The third quadrupole is operated as a mass filter and a spectrum of the resulting ion fragments can be recorded. The limitations of this type of study are pointed out in section 2.3. Enke and co-workers[67] in their publication entitled 'Solving the MS-MS puzzle' discuss the limitations of the triple quadrupole mass spectrometer for structural elucidation via CID studies. The possibility of linking of a triple quadrupole mass spectrometer to a series of computerized libraries of standardised fragmentation patterns of ions has been put forward as the solution to these problems. Computer software has been developed that searches and identifies relationships between parent and duaghter mass spectra, known as the method for analysing patterns in mass spectra (M.A.P.S). A system linking the M.A.P.S software to an empirical formula generator (E.F.G) and a structure generator (GENOA) has been shown to be capable of the identification of di-n-octyl phthalate m/e 300 in a few minutes[68].

A novel development has recently been reported to increase the efficiency of ion molecule reactions occuring in the second quadrupole of a triple quadrupole mass spectrometer[69]. By the application of a positive trapping

potential to the lens plate between the second and the third quadrupole, the time that the reactant ion spends in the second chamber can be increased. Thus the number of reactive collisions of the ion with the neutral molecule is thus increased and hence the yield of product ions increases. The system has been sucessfully used to study the reaction of the methyl cation with acetone[70]. The triple quadrupole mass spectrometer has also been shown to be useful for the rapid determination of carbon monoxide in gas mixtures resulting from the pyrolysis of shale. [71] Carbon monoxide (m/e28) is difficult to distinguish from other ions in a hydrocarbon mixture, the $C_2H_4^+$ ion also has the same m/e value. However by selecting the m/e 28 from the first quadrupole and passing it into krypton in the second selective charge exchange occurs between the carbon monoxide and the krypton. From the peak height corresponding to the Kr^+ ion at m/e 84 the amount of carbon monoxide present may be calculated. A method similar to that described above has also been reported for more routine analysis[72]. The collision cell of a triple quadrupole mass spectrometer is coupled to a GC instrument. An ion of suitable ionization potential is generated and selected using the source and first quadrupole. The ion can then selectively charge-exchange with the particular component of the sample from the GC. The triple quadrupole mass spectrometer is not limited to the detection and study of organic compounds. A triple quadrupole linked to an electrospray ion source and

conditioning chamber has been shown to be useful for the study of multicharged complexes and the thermodynamics of ligand loss[73]. The succesive loss of ligands is studied by dissociation of the complex upon collision with nitrogen in the second quadrupole.

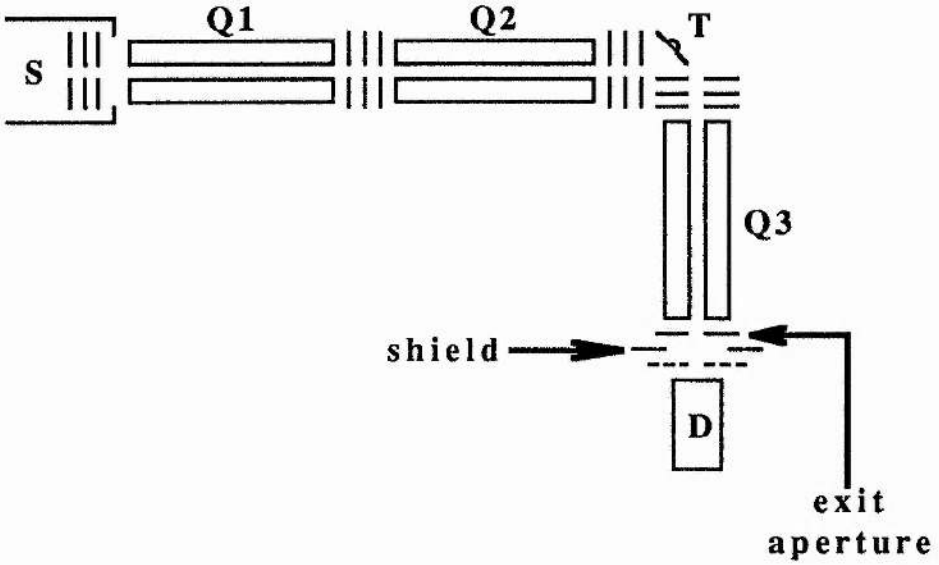


Figure1.14 Triple quadrupole mass spectrometer for SID analysis.

Figure1.14 shows a slightly modified triple quadrupole mass spectrometer[74] which enables the study of surface induced dissociation of molecular ions (SID). The metal target is is situated between the second and the third quadrupoles which are set at right angles to one another.
To date triple quadrupole mass spectrometers have been commercially manufactured by a number of different

analytical companies, and several research institutions have constructed their own instruments.[75,76]

1.40 Other quadrupole mass spectrometer /mass spectrometer combinations

A triple quadrupole mass spectrometer has been coupled with a flowing afterglow apparatus to produce a flow afterglow-TQMS instrument shown in figure1.15[77]. Ions are generated by electron impact in the source and carried by a fast flowing helium plasma. Ion molecule reactions can be studied by the introduction of reagent gases into the helium stream. The ions then pass into the triple quadrupole mass spectrometer where they can be analysed or further reactions can be studied.

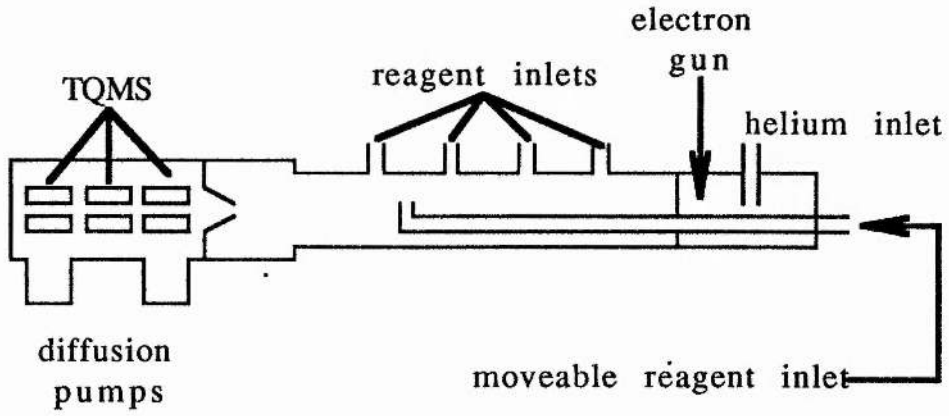


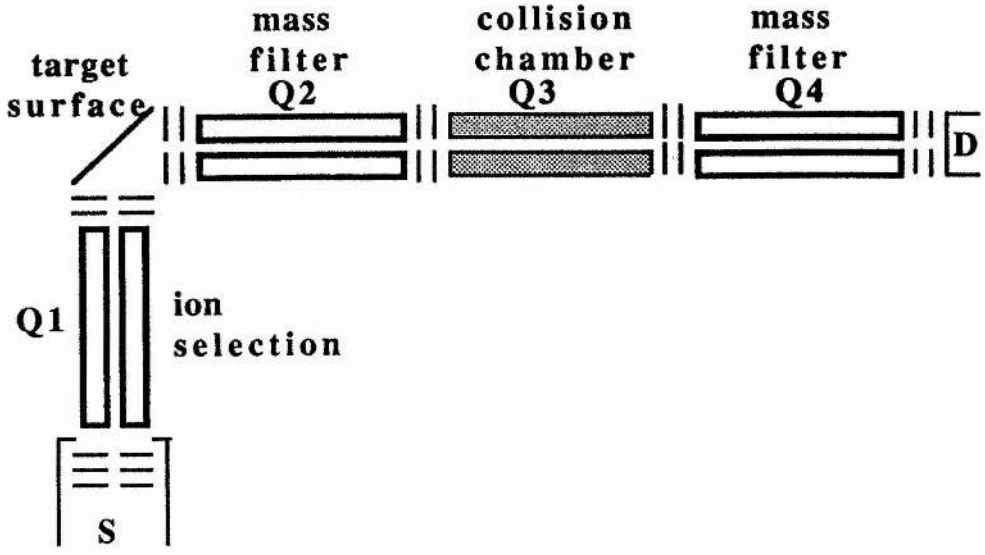
Figure1.15. Flow afterglow/ TQMS instrument.

Glish and Georinger reported the development of a tandem quadrupole-time of flight mass spectrometer[78] The ions are selected using the quadrupole and passed into a collision chamber between the two analysers. Product ions are then analysed using the time of flight sector. This type of combination has the advantage of being considerably cheaper to construct than a triple quadrupole mass spectrometer.

A triple quadruple mass spectrometer which has an interchangable centre quadrupole[79] has also been reported. The instrument may be operated as a conventional triple quadrupole mass spectrometer or alternatively the centre section may be removed and an ion source may be inserted to allow simultanious analysis using both the outer quadrupoles.

A tandem quadrupole fourier transform mass spectrometer has been developed[80]. The incorporation of the first quadrupole of the double quadrupole system allows separation of the ion of interest and the second acts to guide and focus the ions into the magnetic analyser. The quadrupole system prevents too many ions entering the magnetic analyser cell at any given time, thus preventing poor quality spectra due to overloading of the analyser. A tandem quadrupole Fourier transform mass spectrometer has been used in the analysis of samples up to m/e 1000 (ref 81).

1.41 Tetra-quadrupole mass spectrometers



Section may be removed.

Figure 1.16 The tetra-quadrupole mass spectrometer.

Tabet et al have recently developed a tetra-quadrupole mass spectrometer[82] for the analysis of ion structure. It consists of a quadrupole mass filter which allows the selection of a particular primary ion. This primary ion then undergoes surface induced dissociation by collision with a chosen target surface. The resulting products are mass selected by a second quadrupole and reacted or collisionally dissociated in the third quadrupole and the products are mass analysed in the fourth quadrupole. The instrument is versatile in that it may be easily converted back to a normal triple quadrupole mass spectrometer[83].

1.42 Quinquaquadrupole mass spectrometer

The development of the Quinquaquadrupole Mass Spectrometry will be described fully in Chapter 4. Multi-quadrupole mass spectrometers are being developed in France and Australia[84]. However to date no publications have appeared describing spectrometers of this type other than the instrument developed at the University of St Andrews[85,86].

1.43 The quadrupole ion trap.

The Quadrupole Ion Trap was first reported by Paul in 1953[87] Figure 1.17 shows the cross section of this type of instrument.

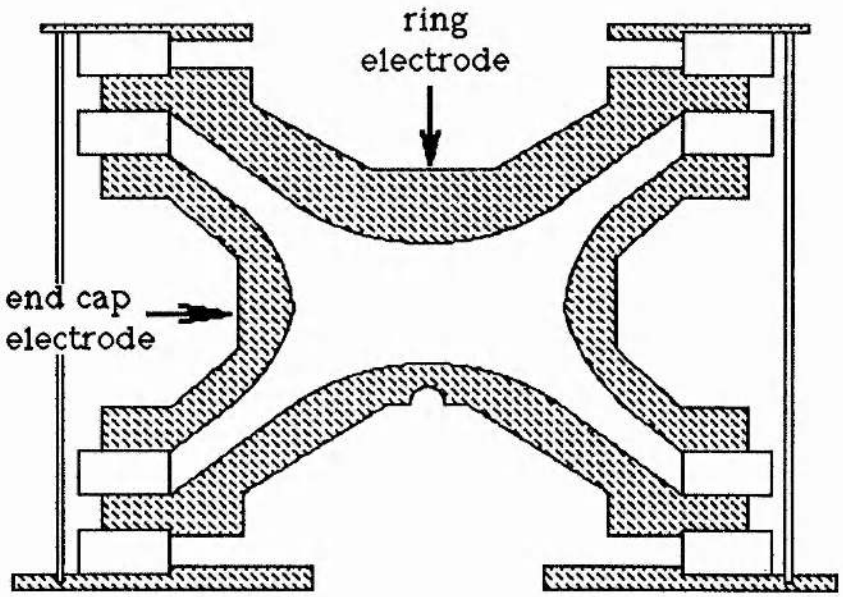


Figure1.17 The quadrupole ion trap.

The quadrupole ion trap operates in a similar way to the conventional quadrupole. A pair of quadrupole electrodes are joined together to form a single ring electrode. The other two electrodes form two end cap electrodes. The field is generated by application of rf/dc voltages to the ring electrodes and end capping electrodes

Ions are generated in the trap by the injection of an electron beam through a small hole in one of the electrodes. The sensitivity of the ion trap for mixture analysis is illustrated by a report of organic compound detection at parts per billion level in well water samples without any pre concentration[88]. Ion traps have also shown to be useful for MS-MS studies[89].

1.44 Quadrupole ion trap /quadrupole combinations

Todd and co-workers have developed a tandem mass spectrometer employing a Quadrupole Ion Trap with a Quadrupole Mass Filter[90]. The trap allows the storage of ions created by electron impact ionization for a period of time-hence the name of the instrument, QUISTOR or QUADRUPOLE ION STORE. The instrument has been used to study the kinetics of ion-molecule reactions and can also be used to perform both CID and ion molecule reaction studies[91,92].

1.45 Other applications of quadrupoles.

In recent years the interactions of ions with solid surfaces has received considerable attention. Techniques such as Electron Induced Desorption (EID)[93], Field Ionization Mass Spectrometry (FIMS)[94] and Secondary Ion Mass Spectrometry (SIMS)[95] all employ quadrupole filter systems. The quadrupoles employed in EID studies are able to "capture" ions over a wide range of angles from the surface under study. SIMS analysis employs quadrupole systems because they are unaffected by a wide energy spread of secondary ions.

1.5 Ion cyclotron resonance spectroscopy.

Ion Cyclotron Resonance Spectroscopy has been used extensively for the study of ion-molecule reactions[96,97]. In recent years it has been largely superseded by the use of multi-quadrupole mass spectrometers.Figure1.18 shows an ICR cell

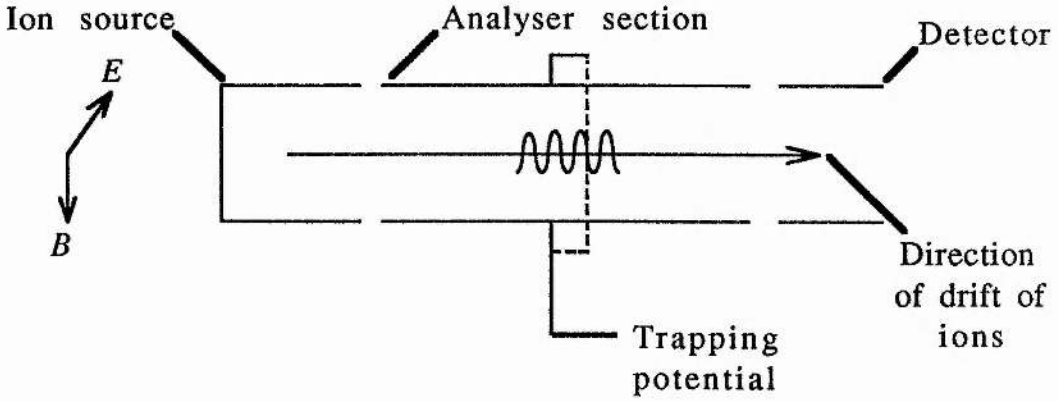


Figure 1.18. Ion Cyclotron Resonance Cell.

Ions are subject to crossed electric and magnetic fields in the cell. They describe cycloidal pathways, which vary accordingly to the mass of the ion and the magnetic and electric field strength. A trapping potential is applied to prevent the ions drifting to the walls of the cell. The time of flight of an ion is relatively long hence there is a high possibility of ion-molecule reactions being observed. The cell is operated by placing it between the faces of a magnet with its axis perpendicular to the magnetic field. During operation the cell is enclosed in a vacuum chamber which is pumped.

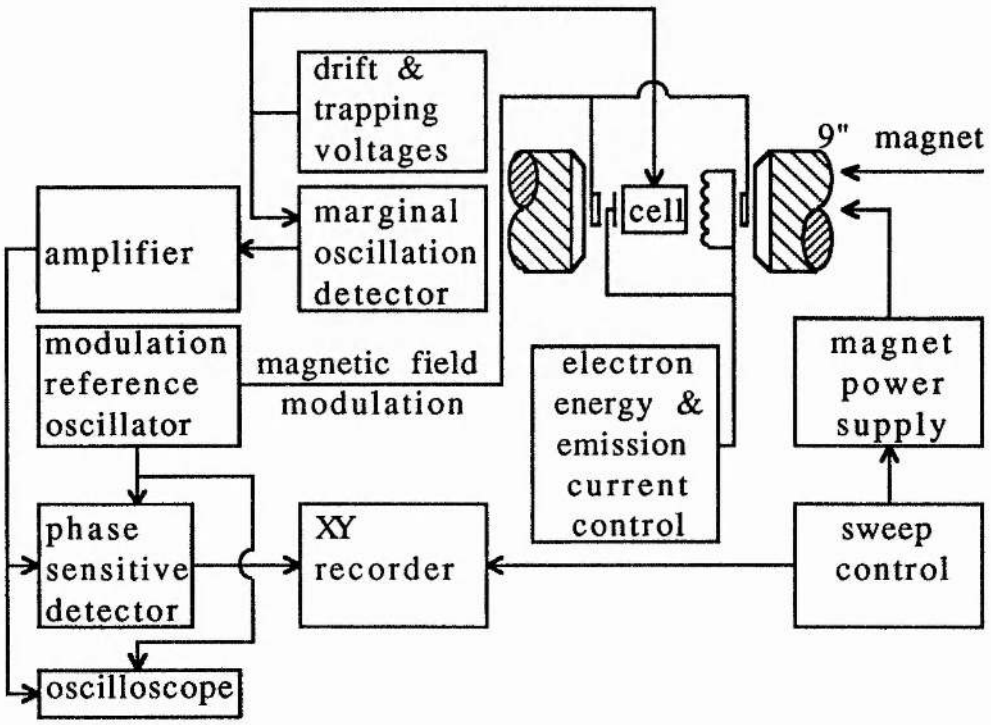


Figure 1.19.

The use of ion cyclotron resonance spectrometers for the study of ion molecule reactions has been extensively reported[96,97].

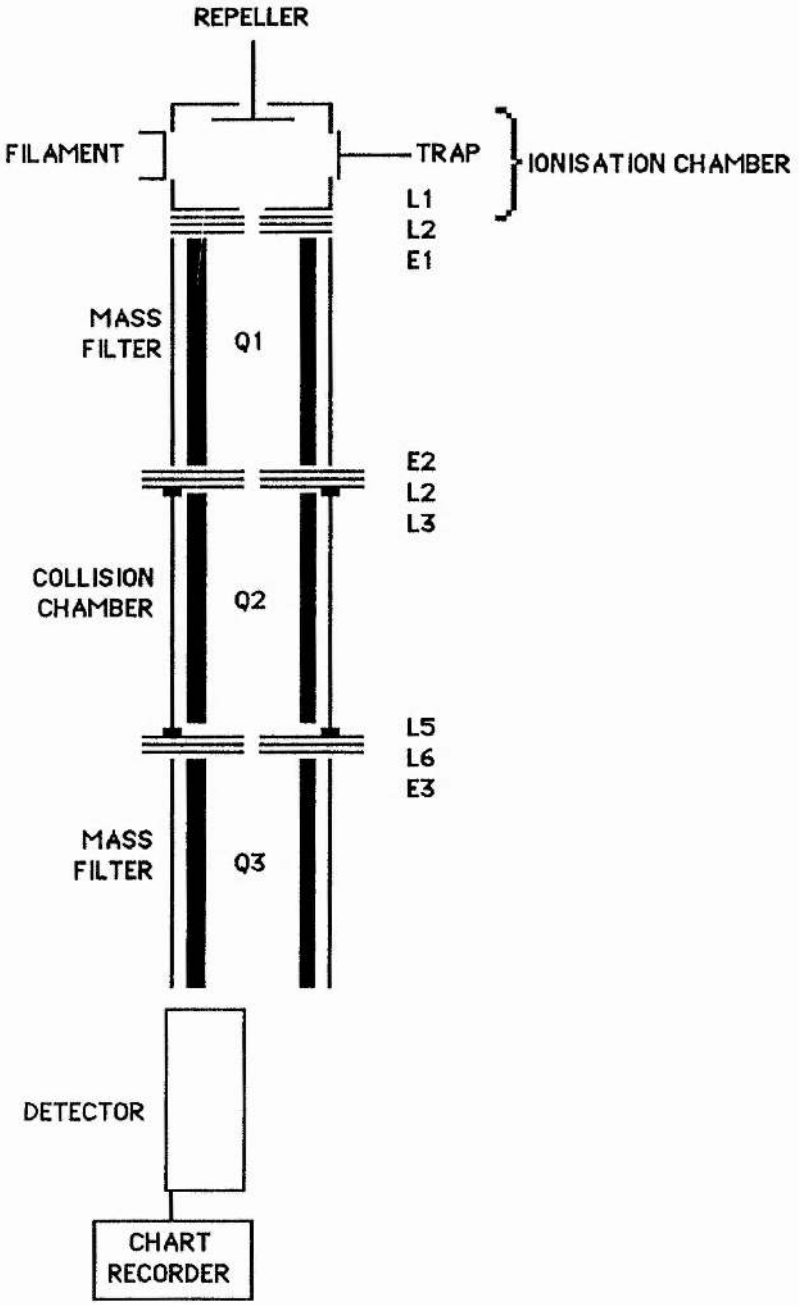
Chapter two.

Experimental section. The use of the triple quadrupole mass spectrometer is described.

n.b This chapter also serves as an experimental chapter for the use of the quinquadrupole mass spectrometer.

2. The Triple Quadrupole Mass Spectrometer (T.Q.M.S).

2.10 Introduction.



The instrument (figure 2.1) was built by VG gas analysis Ltd, Aston Way, Middlewich, Cheshire and was based on the design of Yost, Enke, McGilvery and Morrison[56] . It consists of three standard V.G. QXK300 quadrupole mass spectrometers coupled in series. The rods are of length 125 mm and diameter 6.32 mm. The total mass range of the instrument is 10 to 300 amu.

Ions are generated by electron impact in the ionization chamber. The ions are focussed by three lens plates with varying negative potentials on them. They then pass into the first quadrupole. The first quadrupole is operated as a mass filter and allows any one ion of a particular mass to be selected and passed through to the second quadrupole. The second quadrupole operates as a reaction chamber. The rods are subject to rf only and thus all ions produced pass into the third quadrupole. The ions generated by reaction in the second quadrupole are mass analysed in the third quadrupole which again acts as a mass filter. The ion currents are detected and can be either displayed on an oscilloscope or chart recorder as a series of peaks.

2.11 Pumping and pressure measuring.

The system was pumped using an Edwards oil vapour diffusion pump, fitted with a V.G. NCT4 cold trap and backed by an Edwards E2M8 rotary pump. Pressures are measured in terms of the total pressure inside the apparatus using an

ionization gauge (V.G. VIG23) which is located above the diffusion pump in the main vacuum chamber. The pressure inside the collision chamber can be measured directly using a Penning head connected to a side tube situated within the collision chamber.

2.2 Sample handling.

The samples are admitted to the triple quadrupole mass spectrometer by means of a vacuum line. The procedure for introduction of samples is as follows:

2.20 Gaseous samples.

Suitable primary ion source gases were selected by consultation of the Eight Peak Index Data Book[98]. In some cases a gas producing a large ion current of an ion of particular interest was avoided for various instrumental reasons and a more suitable ion source was used in preference.

Gaseous samples were attached to the vacuum line using quickfit gas sampling tubes. These tubes were of varying size and were filled with gas samples from lecture bottles fitted with gas regulators with rubber tubing Refer to figure 2.2.

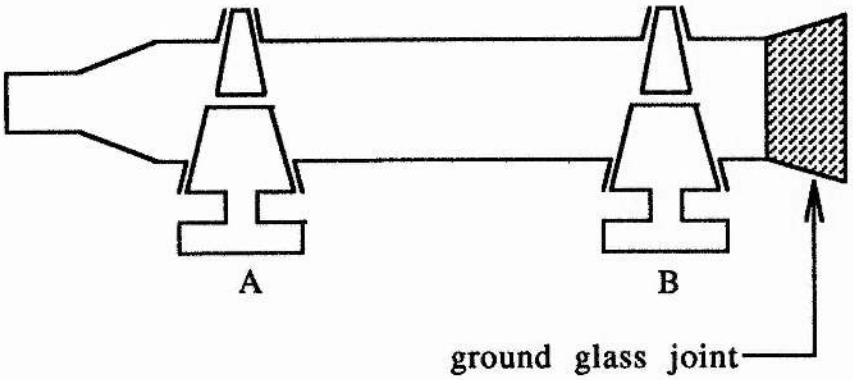


Fig 2.2 Gas Sampling Tube.

Both taps on the sampling tube were initially opened and the sample gas was allowed to flow through the tube thus flushing out the air. Tap **B** and the regulator valve were then closed followed by tap **A**. The sample tube was attached to the vacuum line. Care was taken to grease the joint between the gas sampling tube and the vacuum line only very lightly as an excess of grease would cause impurities to enter the system as sample gases are absorbed and retained in the vacuum grease.

2.21 Use of Peroxides.

The experiments involving the use of tertiary butyl hydrogen peroxide as a primary ion source for OH^+ were carried out using the following extra safety precautions due to the instability and explosive nature of the peroxide:

A. The peroxide was handled at all times with gloves and at a temperature below O °C. A shield was placed around the tube containing the peroxide in case of explosions.

B. Only fractional amounts were used (<0.5 cm^3).

C. At no time was the peroxide allowed to warm to room temperature.

D. The peroxide was disposed of by diluting with an excess of water.

2.22 Liquid samples.

A degassing procedure was required when liquid samples were used. A cold finger was filled to a depth of approximately 2 cm^3 and attached to the gas line. The sample was then frozen using a flask of liquid nitrogen. While still frozen the tap between the cold finger and the vacuum line was opened and the dissolved air from the sample pumped away. The tap was closed, the liquid nitrogen removed and the sample allowed to return to room temperature. The procedure was repeated until no more air could be removed from the sample.

The use of liquid samples as primary ion sources was minimized as it was found that the vapour from liquids such

as tetrachloromethane, methanal and the alcohols tended to condense at the needle valve. This resulted in erratic pressure fluctuations during the course of an experiment. It was found that the use of a heating coil wrapped around the needle valve at a temperature of approximately 40° C minimized this problem. However the warming of the needle valve was undesirable.

2.3 Data Acquisition.

Experiments were carried out over a wide pressure range and the spectra were recorded after each increase in pressure. Care was taken to manually scan the spectrum before recording it. This allowed the correct attenuation to be selected and if possible all product peaks remained on scale, thus making data interpretation easier. The primary ion peak was always off scale during the recording. At the end of each run the peak was attenuated until it was on scale and a recording made.

Great care was taken when calibrating spectra as a mistake in marking the peaks would make all the assignments incorrect. It was essential to calibrate at least in duplicate to ensure correct peak assignment. Great care was also taken when calibrating peaks with m/e>100. It is known that the linearity is lost above m/e 100 due to non linearity of the precision rectifier. The amount of each ion present in

the spectrum was determined by measuring the peak height and multiplying by the attenuation. The percentage of each ion was then calculated using the following formula:

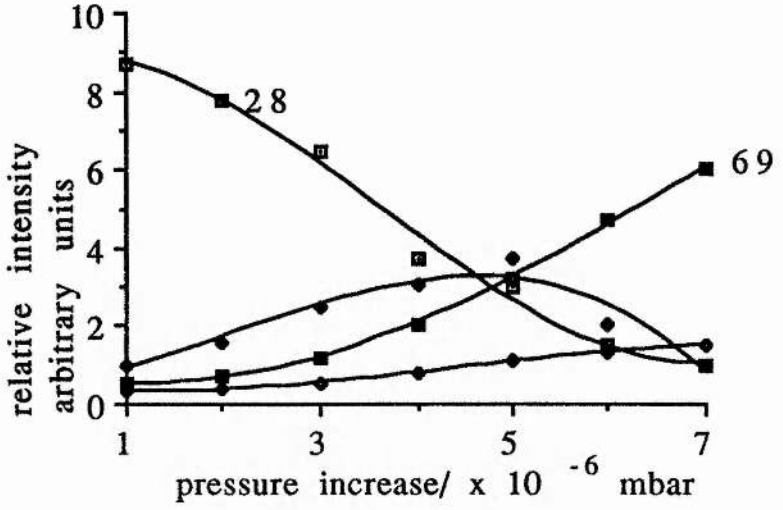
For peak one:

$$\%\ Total\ ion\ flux = \frac{\text{Peak height x Attenuation(peak1)}}{\text{peak height x Attenuation(peaks 1,2,3..n including the primary ion.)}}$$

This gives a measure of the extent of the reaction:

$$\%\ Secondary\ ion\ flux = \frac{\text{peak height x Attenuation(peak1)}}{\text{peak height x Attenuation(peaks1,2,3..n excluding the primary ion).}}$$

This gives a measure of the relative amount of each individual product ion. A graph of secondary ion current against pressure for all the fragments can then be plotted; a typical plot is shown in graph 2.1. When examining a particular series of ion molecule reactions the primary ion and target gas pressures at which spectra were recorded were as similar as possible to allow direct comparison between systems to be made.



Graph 2.1. Typical plot of pressure increase against ion current for an ion molecule reaction.

It can be seen that an indication of reaction pathways leading to secondary and tertiary product ions can be gained from this plot. Taking the above example, as the pressure of target gas is increased the amount of ion of m/e 69 increases and correspondingly the amount of ion of m/e 28 decreases. It can therefore be inferred that ion 69 is derived in some way from ion 28. Further evidence that ion of mass 69 is derived from the reaction of the ion 28 with the neutral gas can be obtained using the following procedure;

SOURCE.	GAS x .
QUAD ONE.	ION x^+ .
QUAD TWO.	**Target gas .**
QUAD THREE.	PRODUCT IONS .

Using this set up the the ion m/e 28 is generated in the source chamber by electron impact and selected in the first quadrupole. It is then reacted with the target gas in the second quadrupole and the fragments analysed in the third. If ion m/e 69 is present in the resulting spectrum it is further evidence to suggest that in the particular reaction ion m/e 69 is derived from the reaction of ion m/e 28 with the target gas. It is however not unambiguous and information about the relative contribution of the reaction of ion 28 with neutral gas to the total ion flux of 69 cannot be obtained.

2.4 Instrumental problems.

A great advantage of the triple quadrupole mass spectrometer over other mass spectrometers is its durability. Only minor instrumental problems were encountered, the most common being filament burn out (about every 6 weeks) and occasional leaks in the vacuum system.

The other problems encountered using the triple quadrupole mass spectrometer were in the main easily rectified. However it was found that the following points had to be borne in mind for accurate results:-

A. It was found that the best results were obtained when operating the instrument at maximum total pressures of the

order of $5x10^{-5}$ mbar. Occasionally reactions were studied at higher pressures above $1x10^{-4}$ mbar. In some cases this resulted in the drown out of signals; signal heights diminished and the multiplier began to give spurious results.

B. In order to observe all product ions the instrument was operated at a relatively high gain when recording spectra ($1X10^{-9}$ A). Any ions present in a spectrum which were off scale were recorded at a different gain setting.

C. The vacuum line was completely dismantled and cleaned at regular intervals to avoid the build up of vacuum grease in the system, since this build up was found to retain a "memory" of previous gases used. All taps were cleaned and replaced. The ion source was also cleaned periodically when replacing the filament. Another area where system contamination occured was at the needle valves. Build up of grease at the taps resulted in erratic pressure fluctuations. This was rectified by periodically stripping the taps and cleaning the needle valves.

D. At regular intervals the instrument was purged with nitrogen to "flush" out any waste gases remaining.

E. The rotary pumps were dismantled, cleaned and re-charged with oil at regular intervals. They were also regularly ballasted.

The triple quadrupole mass spectrometer is shown in figure 2.3 and photograph 1.

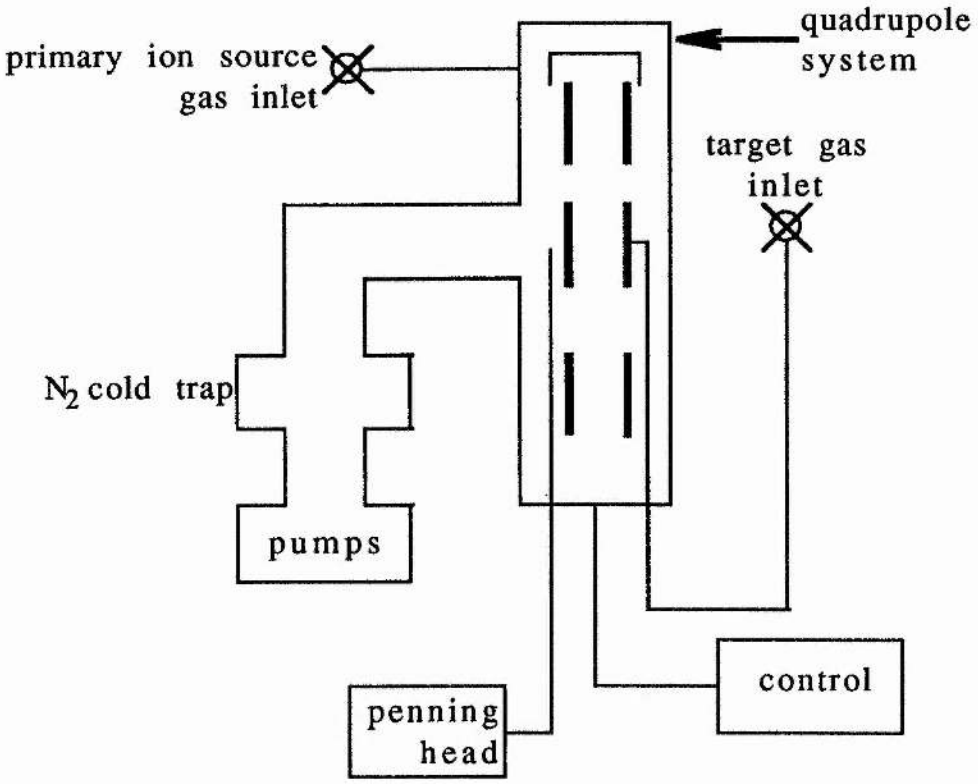
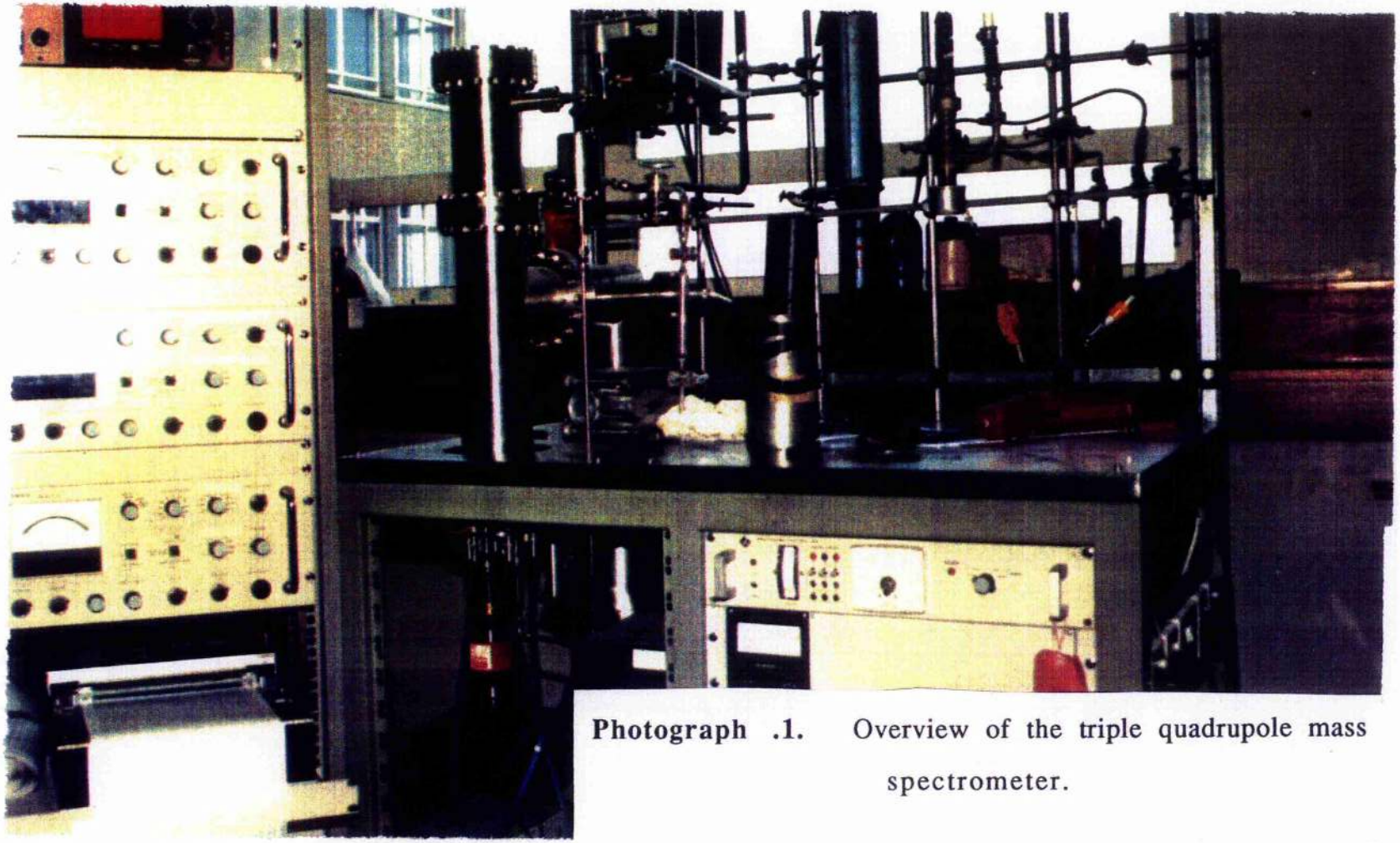


Figure2.3 Overview of the triple quadrupole mass spectrometer including the pumping system.



Photograph .1. Overview of the triple quadrupole mass spectrometer.

Chapter three.

The study of ion molecule reactions using the triple quadrupole mass spectrometer.

The reactions of CX^+ and CX_2^+ ions (where x=H, Cl or F) with linear alkanes and alkenes.

3.The reactions of CX^+ and CX_2^+ where X = H, Cl or F with linear alkanes.

3.10 Introduction.

A number of studies of the reactions of $[CH_3^+]$ and $[CH_4]^+$ saturated with unsaturated hydrocarbons have been undertaken using a variety of techniques[99,100]. Ion molecule reactions of this type lead primarily to the formation of secondary and tertiary ions of higher molecular weight.

Investigations undertaken using the triple quadrupole mass spectrometer focused on the reactions of smaller ions of the form CX^+ and CX_2^+ where X= H, Cl or F with both saturated and unsaturated linear alkanes and alkenes. The pressure of the target gas was kept constant at $1X10^{-5}$ mbar throughout all the investigations.

The ion source gases used were as follows:

CF^+, CF_2^+ and CFH^+ from difluoromethane.

CH^+ and CH_2^+ from methane.

$CFCl^+$ from dichlorodifluoromethane.

3.2 The reactions of CX^+ where X = H, F or CL with C_2 to C_4 linear alkanes.

3.20 CX^+ with ethane.

The principal product ions from the interaction of CX^+ cations with ethane are listed in Table 3.1. (n.b. The

numbers indicate the % ion current of the major product ions.). A * indicates that the ion is also present and amounts to <10% of the total secondary ion flux.

m/e	14	15	26	27	28	29	32	39	41	43	48
Reaction											
CF^+/ethane				*	*	**22**	**30**	*	*	*	
CCl^+/ethane			*	*		**19**		*	*	**19**	**9**
CH^+/ethane	**15**	*	*	*	**28**	**17**		*	*	*	

Table3.1 The reaction of CX^+ with ethane.

The principal processes occuring in each case are the hydrogen atom transfer from ethane and the hydride transfer from the ethane to yield $C_2H_5^+$ and the corresponding carbene.

$$C_2H_6 + CX^+ \longrightarrow C_2H_5 + CXH^+$$
$$C_2H_6 + CX^+ \longrightarrow C_2H_5^+ + CXH$$

The relative amounts of the hydrogen atom transfer product are significantly greater in the CF^+ ion case than in

the other two ion molecule reactions. The reason for this is likely to be that the electron affinity of the CF^+ ion is greater than that of the CCl^+ and CH^+ ions. There is however significantly less difference between the relative amounts of $C_2H_5^+$ ion produced in the CCl^+ and CH^+ ion molecule reactions although the CCl^+ ion has a greater electron affinity. This smaller difference may be attributed to a steric effect due to the relative size of the chlorine atom.

As the pressure of ethane is increased in each of the cases the hydride transfer product ion dominates. The explanation is that the $C_2H_5^+$ ion is collisionally stabilized at higher pressures and also the CXH^+ ion reacts with a further molecule of ethane to produce $C_2H_5^+$.

$$CXH^+ + C_2H_6 \longrightarrow C_2H_5^+ + CXH_2\cdot$$

The formation of the $C_3H_7^+$ ion occurs only at high pressures of ethane; it is formed by the reaction of $C_2H_5^+$ with a further molecule of ethane:

$$C_2H_5^+ + C_2H_6 \longrightarrow [C_4H_{11}]^{+*} \longrightarrow C_3H_7^+ \quad CH_4$$

The $C_3H_5^+$ and $C_3H_3^+$ ions are formed as a result of collision induced dissociation of the $C_3H_7^+$ ion:

$$C_3H_7^+ \longrightarrow C_3H_5^+(H_2) \longrightarrow C_3H_3^+(H_2)$$

It is interesting to note that the total current of secondary ions in the CF^+/ethane ion molecule reaction is significantly greater than in the CH^+/ethane case, but the number of different fragments ions produced is much less. The possible fragmentation pathways are shown below.

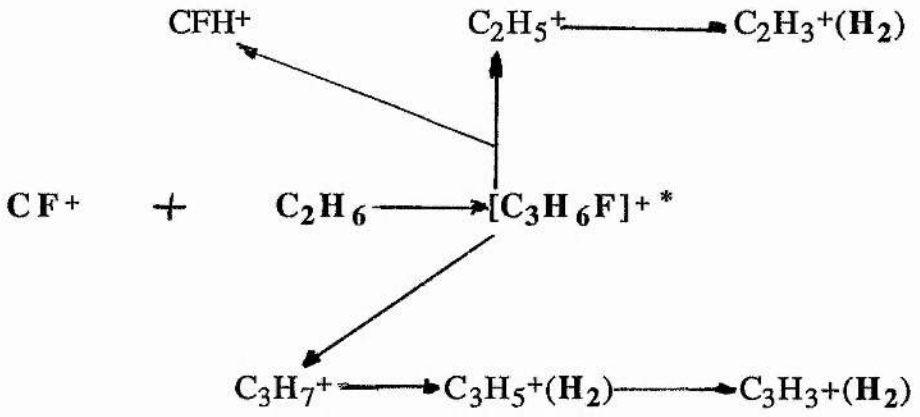


Figure3.1 Ethane with CF^+

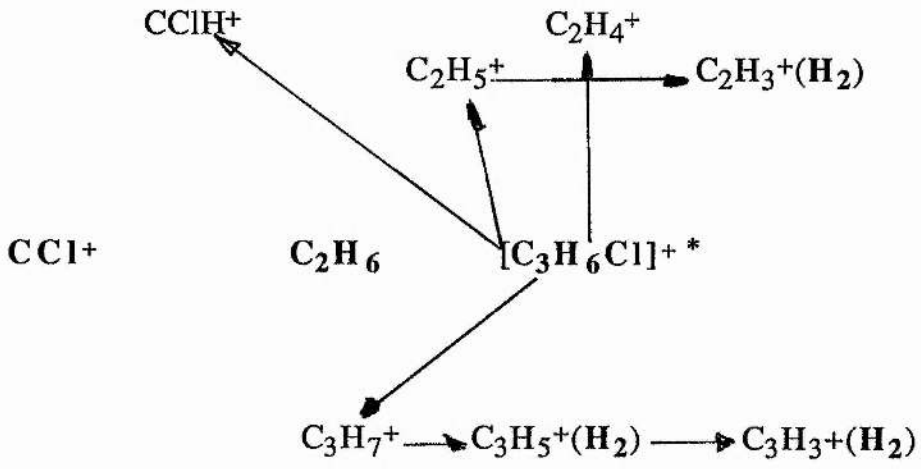


Figure3.2 Ethane with CCl^+

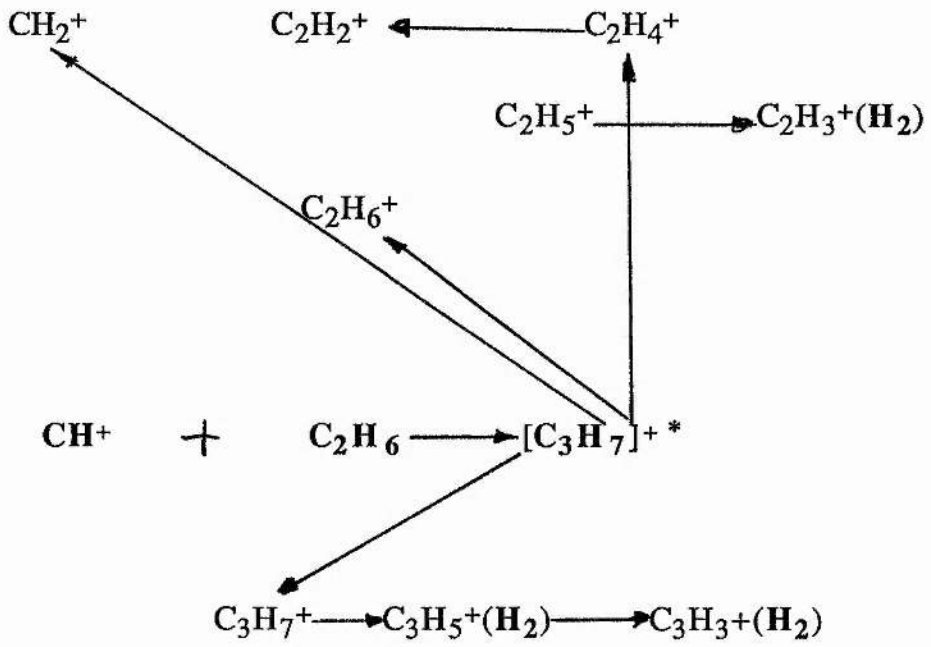


Figure 3.3 Ethane with CH^+

3.21 CX^+ with propane

m/e	14	15	27	28	29	32	39	41	43	48
Reaction										
CF^+/propane	*	*	*	*	*	30	7	25	37	*
CCl^+/propane	*	*	*	*	*	*	5	35	22	6
CH^+/propane	10	*	9	*	12	*	5	18	25	*

Table3.2 The reaction of CX^+ with propane.

The results shown in Table3.2 show that as in the ethane/CX^+ cases there are two principal reaction pathways occuring:

1. $CX^+ + C_3H_8 \longrightarrow [C_4H_8X]^{+*} \longrightarrow C_3H_5\cdot + CXH^+$

2. $CX^+ + C_3H_8 \longrightarrow [C_4H_8X]^{+*} \longrightarrow C_3H_5^+ + CXH\bullet$

As in the ethane/CX^+ studies there is significantly more formation of the $C_3H_7^+$ corresponding to hydride transfer ion in the CF^+/propane case than in the other two corresponding reactions. Again the CXH^+ ion is formed in all cases, however it only occurs in significant amounts in the CF^+/propane case. Minor tertiary product ions can be observed at m/e 55, 57, 67 and 69 as the pressure of propane is increased. These can possibly be attributed to the further reaction of the $C_3H_5^+$ and/or the $C_2H_5^+$ ion;

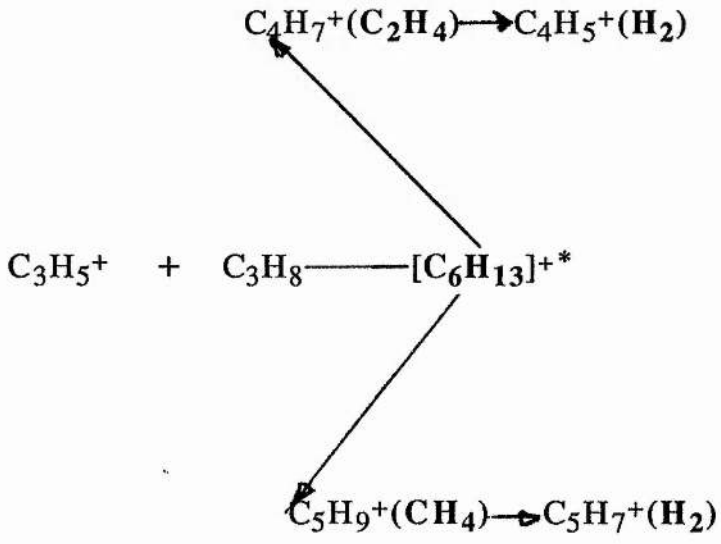


Figure3.4. $C_3H_5^+$ with propane

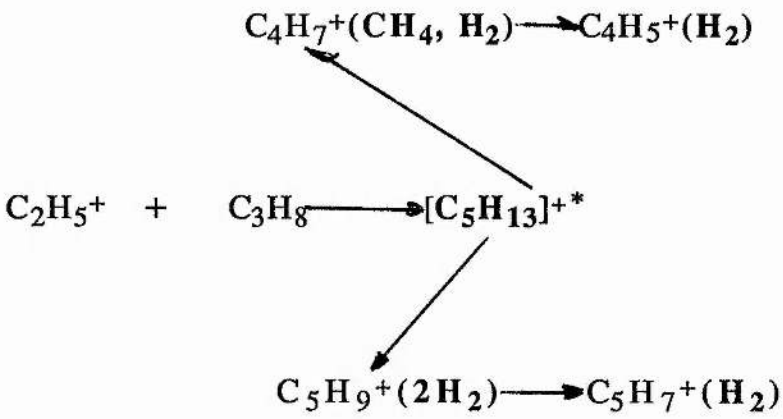


Figure 3.5. Tertiary product ion formation in the propene/CX^+ ion molecule reactions.

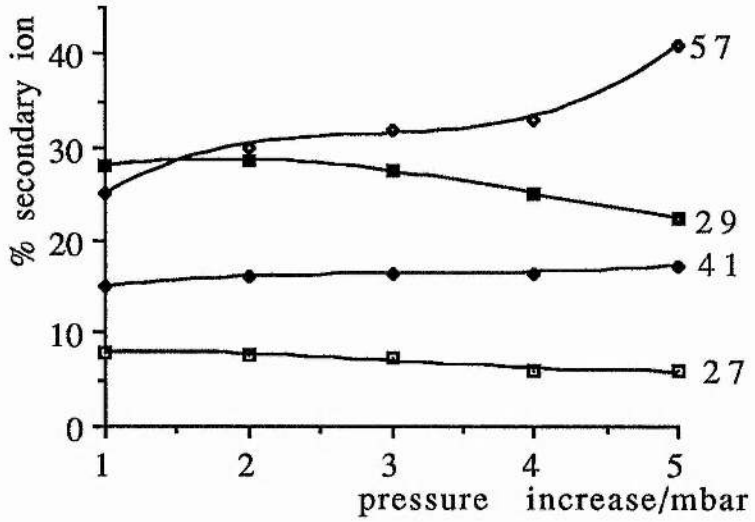
It is not possible to determine the exact routes to these tertiary ions without the quinquaquadrupole mass spectrometer. Both the $C_3H_5^+$ and $C_2H_5^+$ ion fluxes decrease with increasing propane pressure,

3.22 CX^+ with butane.

m/e	27	28	29	32	39	41	43	48	57	58	67
Reaction											
CF^+/butane	5	*	5	27	9	12	*	*	45	*	* *
CCl^+/butane	4	*	9	*	7	9	*	29	34	*	* *
CH^+/butane	*	*	11	*	*	15	*	*	35	19	* *

Table3.3 The reaction of CX^+ with butane.

The ion at m/e 57 corresponding to the $C_4H_9^+$ is dominant in all of the CX^+/butane reactions. It is interesting to note that if a plot is made of $C_2H_5^+/C_4H_9^+$ ion current against increase in butane pressure the following is observed.



Graph3.1. The variation in the ion flux with pressure for the CX+/butane reaction.

This indicates that there is another significant route to $C_4H_9^+$ ion formation is by the reaction of $C_2H_5^+$ with a further molecule of butane.

$$C_2H_5^+ + C_4H_{10} \longrightarrow [C_6H_{15}]^{\pm *} \longrightarrow C_4H_9^+ (C_2H_6)$$

As with the ethane and propane studies the formation of the $C_4H_9^+$ and CXH^+ ions are the two most important processes.

At higher pressures of butane small fluxes of ions up to m/e 85 can be observed. These must be formed by tertiary and higher order processes. It must also be borne in mind that the flux of the $C_4H_9^+$ ion relative to the formation of the $C_3H_7^+$ and $C_2H_5^+$ ions will be higher due to the increasing stability of the cation.

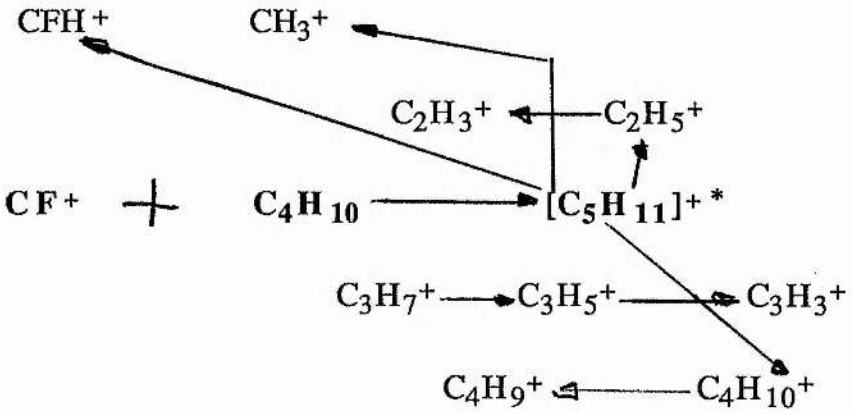


Figure3.6. CF^+ with butane

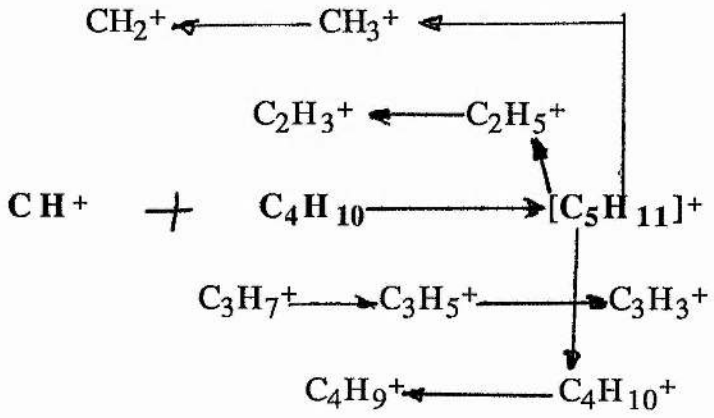


Figure3.7. CH^+ with butane

CClH+

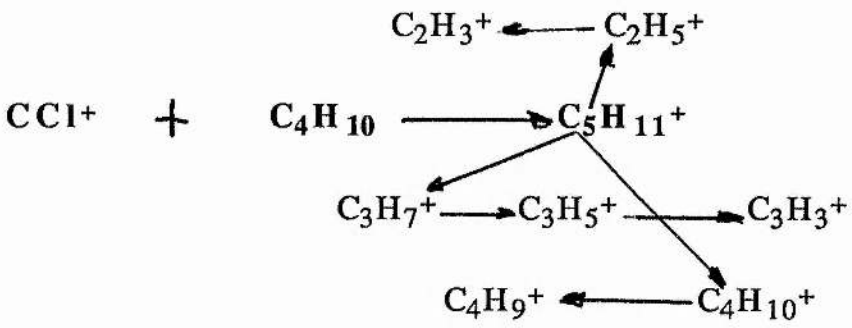


Figure3.8. CCl^+ with butane.

3.3 The ion molecule reactions of CX_2^+ ions with linear alkanes.

3.30 CX_2^+ with ethane.

m/e	15	27	29	30	31	33	39	41	43
Reaction									
CH_2^+/ethane	14	7	40	30			*	*	*
CFH^+/ethane	*	5	19	12	10		*	*	*
CF_2^+/ethane	*	5	55	9	*	*	*	*	*
$CFCl^+$/ethane	*	*	53	12	*		*	*	*

Table3.4. The ion molecule reactions of CX_2^+ with ethane.

n.b. A number of small peaks appeared in the mass spectra of all the ion molecule reactions above at high pressures. Their sizes were insignificant relative to the major ions and are therefore not presented in tabular form. The peaks observed at m/e 55 and m/e 57 increased with increasing ethane pressure. A small decrease was observed in the $C_2H_5^+$ ion flux as the pressure of the ethane was increased, therefore one possible route to the formation of these C_4 fragments could be;

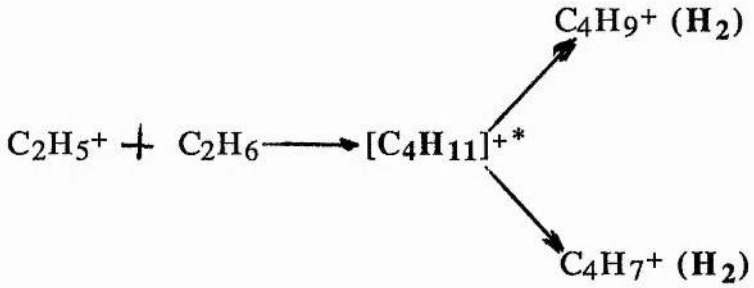


Figure3.9 The reaction of $C_2H_5^+$ with C_2H_6

Charge exchange between the CH_2^+ ion and ethane and the formation of the $C_2H_5^+$ ion are the two major prosseses in the CH_2^+ ethane system. The charge exchange reaction is much less significant in the other CX_2^+/ethane systems. In all cases the $C_2H_5^+$ ion flux decreases with increasing ethane pressure indicating its further reaction. The flux of the $C_2H_6^+$ ion also decreases with increasing ethane pressure. The observation of a large peak at m/e 31 corresponding to the formation of the CF^+ ion in the CF_2^+/ethane case means that at high ethane pressures some of the ion fluxes correspond to the CF+/ethane reaction. The formation of the

CF+ ion in the $CClF^+$/ethane and CFH^+/ethane reactions is also significant.

3.31 CX_2^+ with propane..

m/e	27	28	29	31	32	39	41	43	44	51
Reaction										
CH_2^+/propane	9	17	6	18		*	11	6	30	5
CFH^+/propane	*	*	10	16	5	7	27	17	8	
CF_2^+/propane	*	*	12	19	15	*	19	9	7	5
$CFCl^+$/propane	*	*	*	12	8	*	17	13	7	

Table3.5. The ion molecule reactions of CX_2^+ with propane.

The CX_2^+/propane systems are similar to the CX_2^+/ethane systems. The charge transfer ion is present in varying quantities in all the CX_2^+/propane systems. The dominant ion is in all cases the $C_3H_5^+$ ion which is formed directly from the $C_3H_7^+$ ion. There are three C_4 ions which appear as the pressure of propane is increased. These occur at m/e 55, 56, and 57 and correspond to the $C_4H_7^+$, $C_4H_8^+$ and $C_4H_9^+$ ions of masses 56, 57, and 58 respectively. They are likely to be tertiary products from the further reaction of $C_3H_5^+$ or $C_2H_5^+$

with propane. As the pressure of propane is increased there is a decrease in the $C_3H_5^+$ and $C_2H_5^+$ ion fluxes.

3.32 CX_2^+ with n-butane..

m/e	15	27	28	29	31	39	41	43	57	58
Reaction										
CH_2^+/n-butane	*	*	*	20		*	15	*	29	6
CFH^+/n-butane	*	*	*	22	9	5	7	*	35	5
CF_2^+/n-butane	*	*	*	17	13	7	13	*	33	2
$CFCl^+$/n-butane	*	*	*	11	12	*	8	19	43	*

Table3.6. The ion molecule reactions of $CX_2^+$with butane.

The CX_2^+/butane systems show two major product ions throughout the pressure range studied. In all cases the $C_4H_9^+$ ion is the major product ion. The flux of this ion is at its highest in the $CFCl^+$/n-butane system accounting for appproximately 40% of the total secondary ion flux at n-butane pressures below 5 $x10^{-5}$mbar. Its flux decreases with increasing n-butane pressure, this indicating its reaction to form tertiary ions. Minor fluxes of $C_5H_9^+$ and C_6 ions are also observed at high pressures of n-butane.

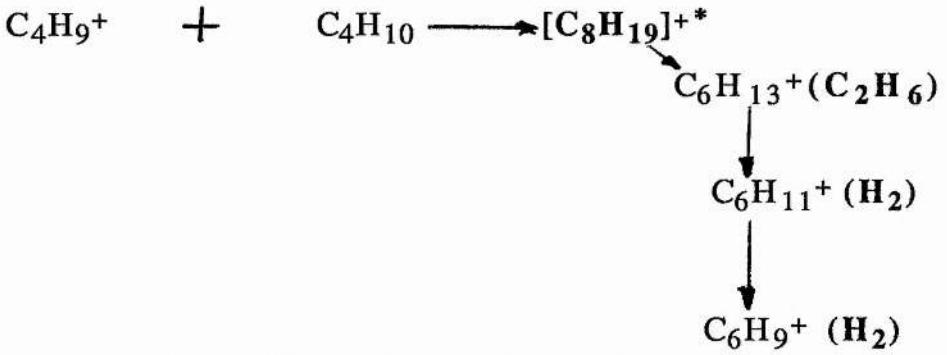
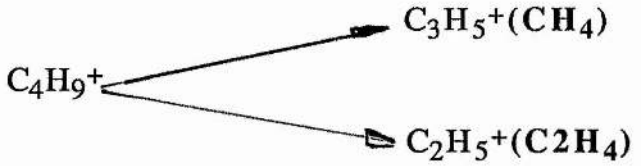


Figure3.10 Formation of the minor ions

The fluxes of all the tertiary product ions, although small, increase with increasing n-butane pressure.

The $C_4H_9^+$ ion must also fragment to give the $C_3H_5^+$ and $C_2H_5^+$ ions



3.3 The reactions of CX^+ ions with linear alkenes.

3.30 CX^+/ethene

m/e	14	27	28	29	32	39	41	48	67	69
Reaction										
CH^+/ethene	*	29	25	*	*	23	31	*	*	7
CF^+/ethene	*	8	12	*	*	22	35	*	*	5
CCl^+/ethene	*	*	18	*	*	17	27	*	*	3

Table3.7. The ion molecule reactions of CX^+ ions with ethene..

It can be seen from the above table that charge exchange between the CH^+ ion and ethene is quite a significant process compared to the other two CX^+/ethene reactions. The ionization potentials of the CH^+ and ethene are 10.64 eV and 10.50 eV[101] respectively. It can be seen from the results in table3.7 that the principle product ion in each of the three CX^+/ethene systems studied is the $C_3H_5^+$ ion. This ion may be formed by either charge exchange to the ethene followed by a further reaction of the ethene radical cation with another molecule of ethene and the elimination of a methyl radical or in the CH^+/ethene case by direct combination of the ion with a molecule of ethene.

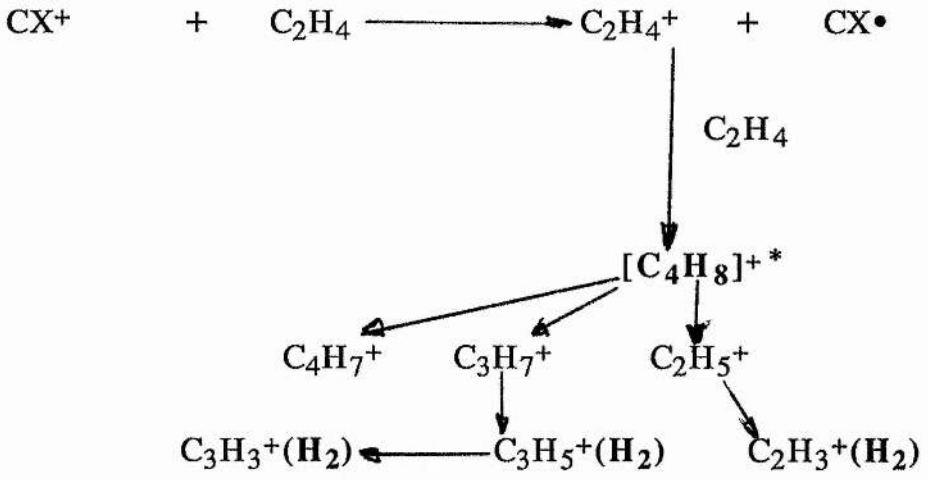


Figure 3.11 Fragmentation route via charge exchange to the principal product ions in the CX^+/ethene ion molecule reaction.

$$CH^+ + C_2H_4^+ \longrightarrow C_3H_5^+$$

Figure3.12. Route to the $C_3H_5^+$ ion via direct combination.

In all the cases the flux of the $C_3H_5^+$ ion decreases with increasing ethene pressure due to further reaction producing the $C_5H_9^+$ ion:

$$C_3H_5^+ + C_2H_4 \longrightarrow C_5H_9^+ \longrightarrow C_5H_7^+ (H_2)$$

Figure3.13. Likely route to the $C_5H_7^+$ and $C_5H_9^+$ ions.

Figure 3.11 also shows the the $C_2H_5^+$ and $C_2H_3^+$ ions. These both occur in high yields initially and their flux decreases with increasing ethene pressure.

3.31 CX^+ with propene

m/e	15	27	28	29	31	33	39	41	42	48
Reaction										
CH^+/ propene	*	10	*	14		*	12	15	25	
CF^+/ propene	*	3	*	7	9	50	5	12	11	
CCl^+/ propene	*	4	*	7		*	7	12	*	19

Table3.8. The ion molecule reactions of CX^+ ions with propene.

The CX^+/propene system is similar to the CX^+/ethene system in that both direct combination of the CH^+ with propene as well as charge exchange followed by tertiary product formation is likely to be occuring. If the process were completely charge exchange a much larger spread of secondary and tertiary fragments would be present in the spectrum (ref chapter 5). Minor ions are observed up to m/e 69 as the pressure of propane is increased; however no higher order ions are observed.

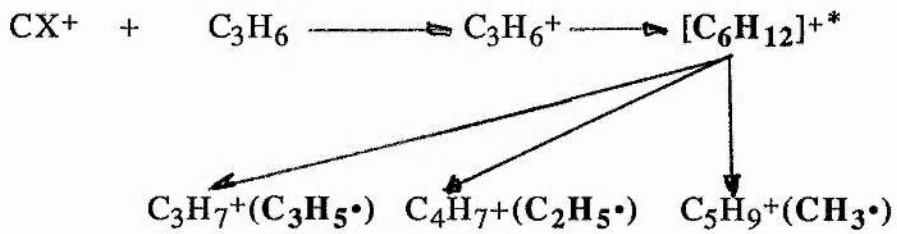


Figure3.14 Reaction of the C3H6+ ion with propene.

3.32 CX^+/1-Butene

m/e	15	27	28	29	32	39	41	55	56	69
Reaction										
CH^+/1-butene	*	11	*	15		6	9	13	17	9
CF^+/1-butene	*	9	*	13	9	5	7	11	9	10
CCl^+/1-butene	*	5	*	8		*	*	18	8	5

Table3.9. The ion molecule reactions of CX^+ ions with1-butene.

In the CX^+/1-butene system the charge exchange product is significant in all cases. Again the flux of this ion decreases with increasing 1-butene pressure indicating further reaction. At high 1-butene pressures very small peaks appear at m/e 70 and 71. These ions could be formed by the reaction of the $C_4H_8^+$ ion with a further molecule of 1-butene.

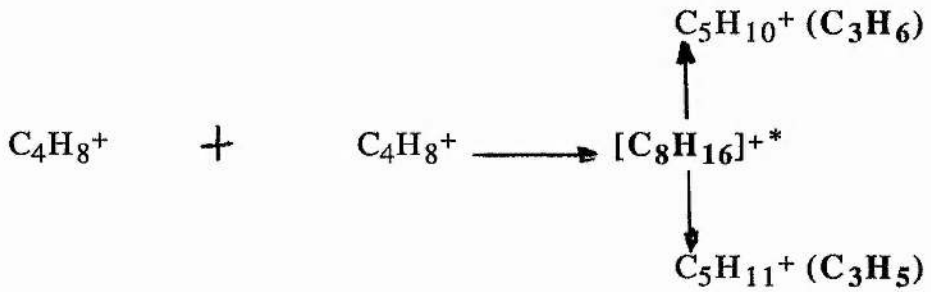


Figure3.15 Formation of minor fragments.

3.4 The ion molecule reactions of CX_2^+ where X=H, Cl and F with linear alkenes.

3.40 Introduction

The reactions of CH_2^+,CHF^+, CF_2^+,$CFCl^+$, CCl_2^+ and $CClH^+$ with linear alkenes have all been examined over a wide pressure range ($1x10^{-6}$ mbar to $1x10^{-4}$ mbar) of target gas pressure. The results of each investigation will be discussed in turn.

3.41 CX_2^+ with ethene

m/e	15	27	28	29	31	39	41	43	53
Reaction									
CH_2^+/ethene	10	18	14	9		22	9	*	6
CFH^+/ethene	*	11	13	7	9	9	14	*	5
CF_2^+/ethene	*	6	24	*	19	7	17	*	9
$CFCl^+$/ethene	*	*	*	*	15	*	16	*	4

Table 3.10. The ion molecule reactions of CX^+ ions with ethene.

The reactions of all CX_2^+ ions with ethene produce the same three major product ions at m/e 41, m/e 27 and m/e 28 corresponding to the $C_3H_5^+$, $C_2H_3^+$ and the $C_2H_4^+$ ions ion respectively. As the pressure of ethene is increased the flux of the $C_3H_5^+$ ion also increases and the flux of the $C_3H_3^+$ ion decreases indicating that the $C_3H_5^+$ ion is being collisionally stabilized. Similar relationships exist between the relative fluxes of the $C_2H_5^+/C_2H_3^+$ ions at m/e 27 and 29 and the $C_5H_9^+/C_5H_7^+$ ions at m/e 67 and 69. The C_5 ions are again produced by the reaction of the $C_3H_5^+$ ion with a further molecule of ethene to produce the $C_5H_9^+$ ion and loss of

hydrogen from this ion to produce the $C_5H_7^+$ ion. Studies on the quinquaquadrupole mass spectrometer have confirmed these routes. It is interesting to note that the $C_2H_4^+$ ion is far less abundant in the CH_2^+/ethene reaction than in the CH^+/ethene case. This can be possibly attributed to the differing ionization energies of the ions. The ionization potentials are CH^+(10.64eV), CH_2^+ (10.5eV) and $C_2H_4^+$ (10.50eV).

As with the other systems studied the $CClF^+$ ion fragments to give a significant flux of CF^+ which must also be reacting with the ethene.

3.42 CX_2^+ with propene

m/e	27	29	31	39	41	42	55	56	57	67	69	83
Reaction												
CH_2^+/propene	5	*		13	28	15	12	*	*	6	9	*
CFH^+/propene	7	*	*	5	23	12	17	*	*	7	10	*
CF_2^+/propene	*	*	11	7	25	11	20	*	*	6	7	*
$CFCl^+$/propene	*	*	20	18	7	15	*	*	*	7	*	*

Table3.11. The ion molecule reactions of CX_2^+ ions with propene.

It seems likely that the reactions of the $C_3H_6^{+\cdot}$ ion with propene contribute to a large amount of the ions produced. It is a significant product ion from all four CX_2^+ systems and the flux of it decreases with increasing propene pressure.

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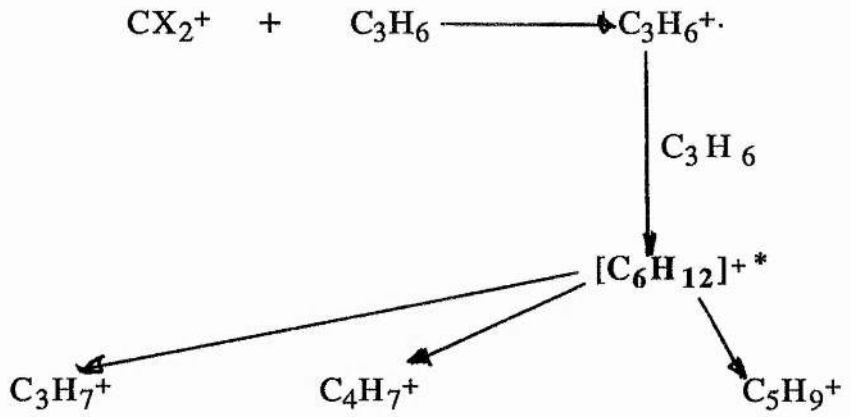


Figure3.16. The reaction of the $C_3H_6^+$ ion to produce the major fragment ions

At high propene pressures small peaks appear at m/e 81 and m/e 83. Although they do not contribute significantly to the total flux of secondary ions they have also been observed in the propenyl cation/propene reaction. The flux of the $C_3H_6^+$ ion at increasing propene pressures indicating a further reaction of this ion.

3.43 CX_2^+ with 1-butene.

m/e	27	29	31	39	41	43	55	56	57	67	69	83
Reaction												
CH_2^+/1-butene	9	*	*	11	*	18	12	9	3	7	*	
CFH^+/1-butene	5	*	15	*	16	*	15	10	3	4	9	*
CF_2^+/ 1-butene	*	*	18	*	*	*	12	16	*	*	10	*
$CFCl^+$/1-butene	*	6	27	*	*	*	*	9	*	2	3	*

Table3.12. The ion molecule reactions of CX^+ ions with 1-butene.

The major ions formed in the CX_2^+/1-butene reactions are the $C_4H_7^+$ ion, the flux of which decreases as the pressure of 1-butene is increased and the $C_4H_8^+$ ion formed by charge exchange. The flux of this ion also decreases as the pressure of 1-butene is increased indicating further reaction. The flux of the $C_3H_5^+$ ion decreases with increased 1-butene pressure. The observed decrease in $C_3H_5^+$ and $C_4H_7^+$ with increased 1-butene pressure may be as a result of further reactions of these ions. Alternatively it may be because the $C_4H_8^+$ ion reacts with another molecule of 1-butene to form the tertiary products present at higher pressures.

There is a relative increase in the fluxes of ions at m/e70, 71,82, 83 and 84. All of these higher order ions could be formed from the reaction of $C_4H_8^+$ with C_4H_8.

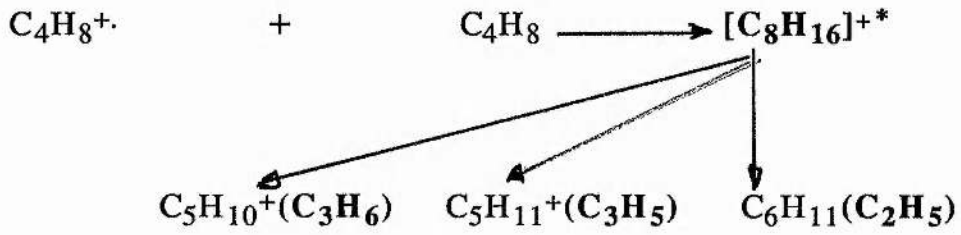


Figure 3.17 Formation of the C_5 and C_6 ions by the reaction of $C_4H_8^+$ with 1-butene.

Chapter four.

The development of the quinquaquadrupole mass spectrometer.

4. THE QUINQUAQUADRUPOLE MASS SPECTROMETER.

4.10 General introduction.

The quinquaquadrupole mass spectrometer is essentially an extension of the triple quadrupole mass spectrometer. Ions are produced from the selected primary ion source gas which is ionized by electron impact in the source. A particular primary ion is then selected by the filtering action of the first quadrupole and passed into the second quadrupole where it collides with a first neutral target gas. The ionic products pass into the third quadrupole which again acts as a mass filter. An ion selected from the third quadrupole is then passed into the fourth quadrupole where it collides with a second neutral target gas. Product ions emerging from the fourth quadrupole are mass analysed using the fifth quadrupole. The individual signals are transmitted to an electron multiplier and may either be displayed on an oscilloscope or recorded on a chart recorder.

4.11 Potential uses of the quinquaquadrupole mass spectrometer

The quinquaquadrupole mass spectrometer has a number of potential uses:

A. The triple quadrupole mass spectrometer allows ion molecule reactions to be studied over a wide range of primary ion target gas pressures. However it does not allow unambiguous determination of the route(s) to a particular product ion. Consider the following reaction which could be carried out on the triple quadrupole mass spectrometer.

QUAD 1

$C_3H_6 + e^- \longrightarrow C_3H_6^{+\bullet} + 2e^-$

QUAD 2

$C_3H_6^{+\bullet} + C_3H_6 \longrightarrow [C_6H_{12}]^{+\bullet *}$

QUAD 3

Analysis of product ion fragments;

m/e 27, 29, 39, 40, **41**, **43**, 54, **55**, 56, 57, 67, 68, **69**, **70**, 71, 81, 83, 84, 85, 97, 98, 99, 111.

(N.B The principal product ions are highlighted.).

In the above reaction scheme, it is not possible to determine if the ion of mass 70 is the result of one or both of the following ion molecule reactions....

1. $C_4H_8^+ + C_3H_6 \longrightarrow C_5H_{10}^+ + C_2H_4$

2. $C_3H_7^+ + C_3H_6 \longrightarrow C_5H_{10}^+ + CH_3$

The quinquaquadrupole mass spectrometer can be used to elucidate the reaction pathways. The major route to the product ion of mass 70 in the above scheme could be determined using the quinquaquadrupole mass spectrometer as follows:

	MOLECULE/ION.
SOURCE.	Propene.
QUAD ONE.	Select $C_3H_6^{+\bullet}$
QUAD TWO.	Propene.
QUAD THREE.	Select $C_3H_7^{+\bullet}$
QUAD FOUR.	Propene.
QUAD FIVE.	Product ions..

Followed by;

	MOLECULE/ION.
SOURCE.	propene
QUAD ONE.	Select $C_3H_6^{+\bullet}$
QUAD TWO.	Propene.
QUAD THREE.	Select $C_4H_8^{+\bullet}$
QUAD FOUR.	Propene.
QUAD FIVE.	Product ions..

The ions produced in each case would clearly indicate the route to the ion of mass 70. If both reactions produced ions of mass 70 then the relative contribution of each route could be assessed. There is a clear advantage of this procedure to the modelling experiments described in previous ion-molecule reaction studies.

B. The quinquaquadrupole mass spectrometer could be used to study the reactions of novel ions which can be produced only by having an initial ion molecule reaction.

	MOLECULE/ION
SOURCE	Methane.
QUAD ONE.	CH_4^+
QUAD TWO.	CH_4
QUAD THREE.	CH_5^+
QUAD FOUR.	Target.
QUAD FIVE.	Product ions..

The above scheme illustrates how the reactions of the methonium ion can be studied. Methonium can only be studied in the triple quadrupole mass spectrometer by introducing a high pressure of methane into the ion source; even then the peak is very small at pressures of methane of 1×10^{-4} mbar. A pure peak of CH_5^+ can be obtained by generating CH_4^+ or a suitable protonating agent, (CH_2N^+ or

CHO^+) from electron impact of a suitable primary ion source gas and reacting it with methane in the second quadrupole. The CH_5^+ can then be selected in the third quadrupole and reacted with a target gas in the fourth quadrupole. The product ions can then be analysed in the fifth quadrupole.

C. Structural information about particular ions can be obtained by setting up the reaction scheme as follows...

	ION/MOLECULE.
SOURCE.	Source gas.
QUAD ONE.	Primary ion.
QUAD TWO.	Target gas.
QUAD THREE.	Product ions.
QUAD FOUR.	Neutral gas.
QUAD FIVE.	Product ions.

The first three quadrupoles act as a triple quadrupole mass spectrometer. Ions selected by the third quadrupole can collide with the neutral gas in the fourth chamber. This will cause collision induced dissociation of the particular ion and the product ions can be analysed in the fifth quadrupole.

Alternatively the quinquaquadrupole could be set up to determine the structural composition of an unknown molecule by colliding individual fragment ions from the unknown with neutral gases in the second and fourth quadrupoles. The first, third and fifth quadrupoles acting as mass filters. This procedure is represented by the figure 4.1.

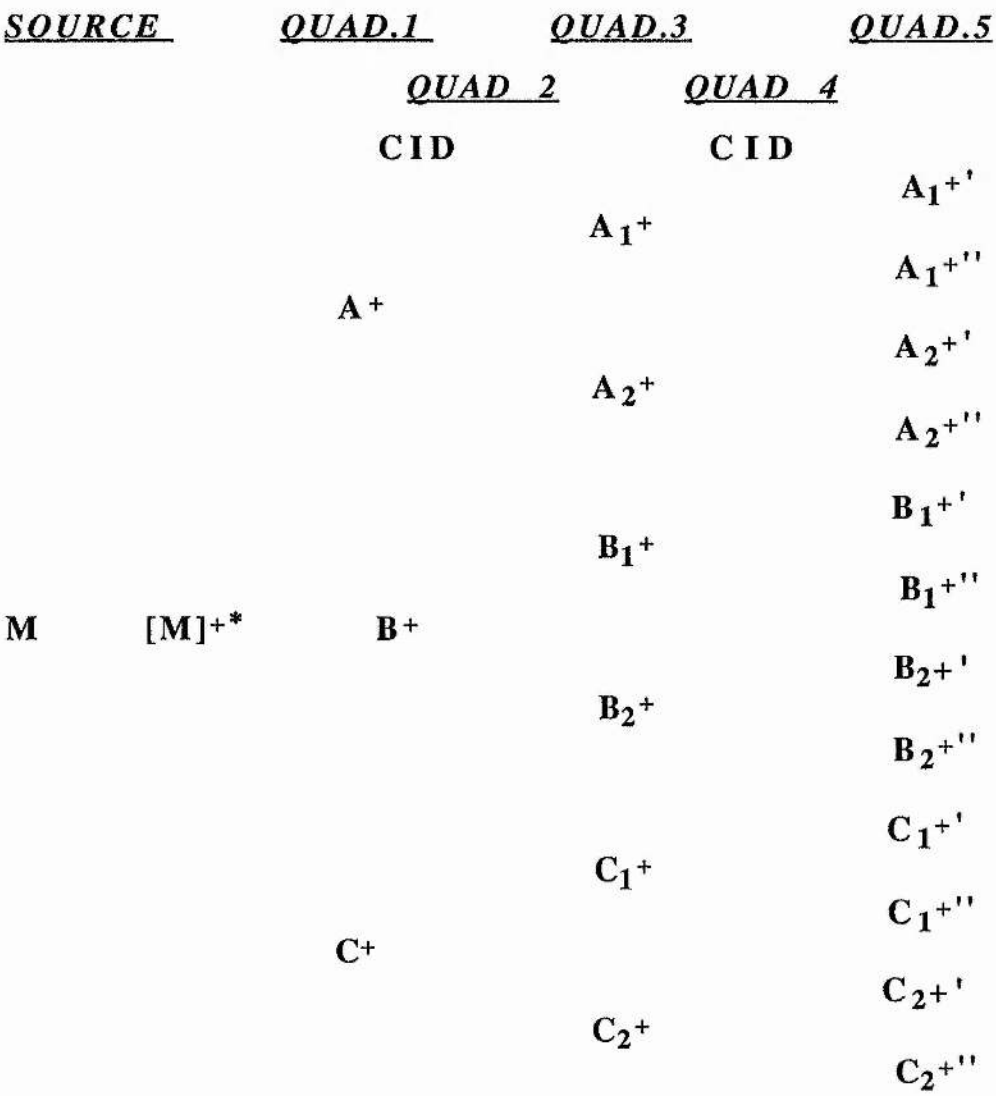


Figure 4.1 CID studies on the quinquadrupole mass

Stage 1.

The first quadrupole is scanned while the other quadrupoles are operated in the rf only mode. This allows a mass spectrum of the sample to be obtained.

Stage 2.

One of the primary ions is then selected and passed into the second quadrupole were it is collisionally dissociated by interaction with a suitable target. Quadrupoles four and five are operated in rf only mode while the third quadrupole is scanned to obtain a spectrum of the fragment ions.

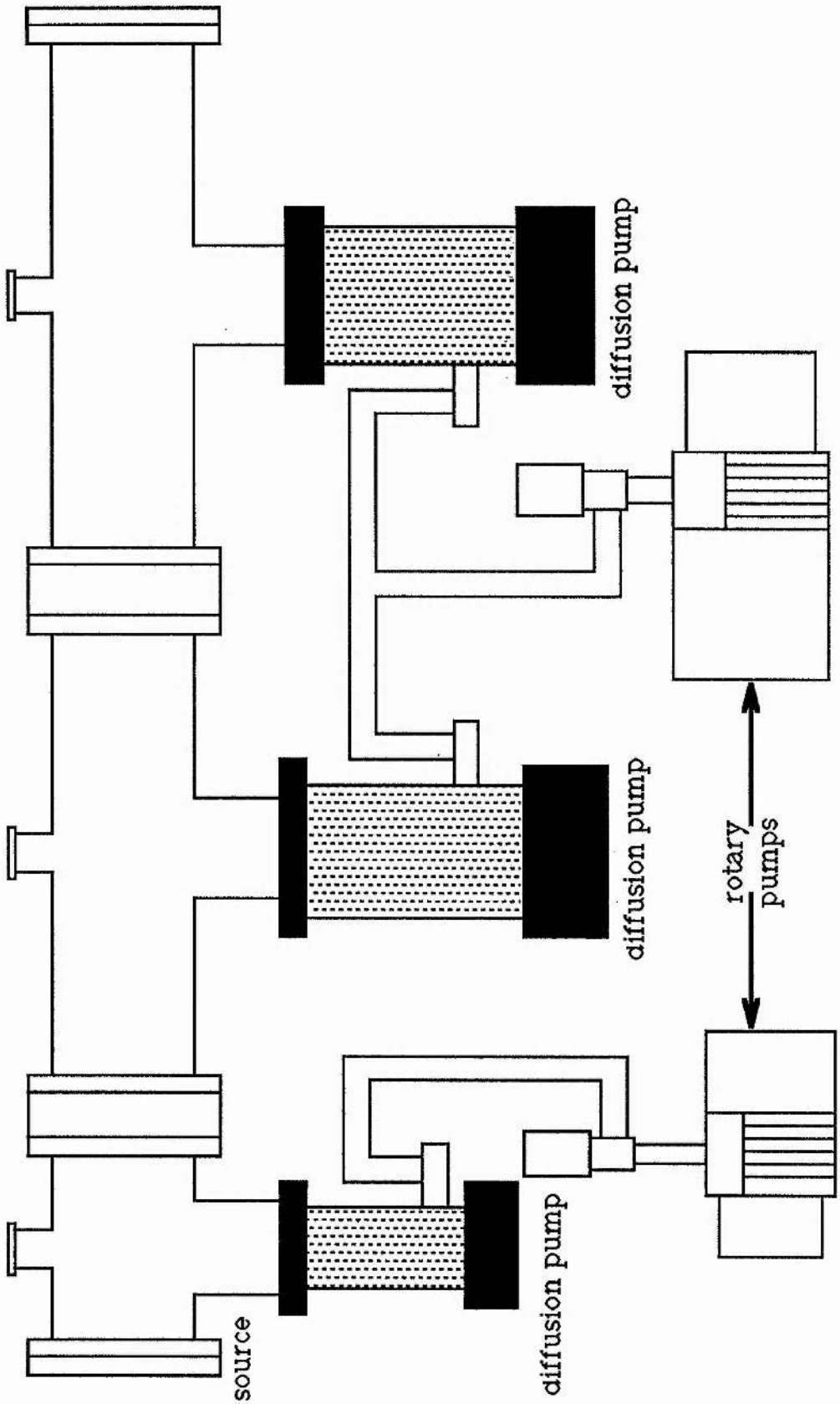
Stage 3.

The third quadrupole is set to transmit one of the secondary ions into the fourth quadrupole were it undergoes further collisional dissociation by interaction with a suitable target. The spectrum of the resulting fragments can then be recorded by scanning the fifth quadrupole.

The three stages can be sucessively repeated, each time setting the first quadrupole to transmit a different primary ion. Structural assignments can then be made using the enormous amount of information obtained adopting this procedure.

Clearly there is a great deal of potential for the quinquaquadrupole mass spectrometer.

This chapter will be concerned with the instrumental design and development. The numerous problems and their solutions will be described.


diffusion pump
diffusion pump
rotary
pumps
diffusion pump
source

4.2 Basic design of the quinquaquadrupole mass spectrometer.

The quinquaquadrupole mass spectrometer was designed and built at St Andrews university. Certain components were obtained from the University of La Trobe in Australia, notably the outer casing and the multiplier. The senior electronics technician at St Andrews designed and built the electronics circuits. The circuits followed as far as possible those of the triple quadrupole mass spectrometer. A schematic diagram of the instrument showing the pumping is shown in figure 4.2. A block diagram of the components is also shown in figure 4.3.

n.b. Photographs of the instrument are also presented in the appendix.

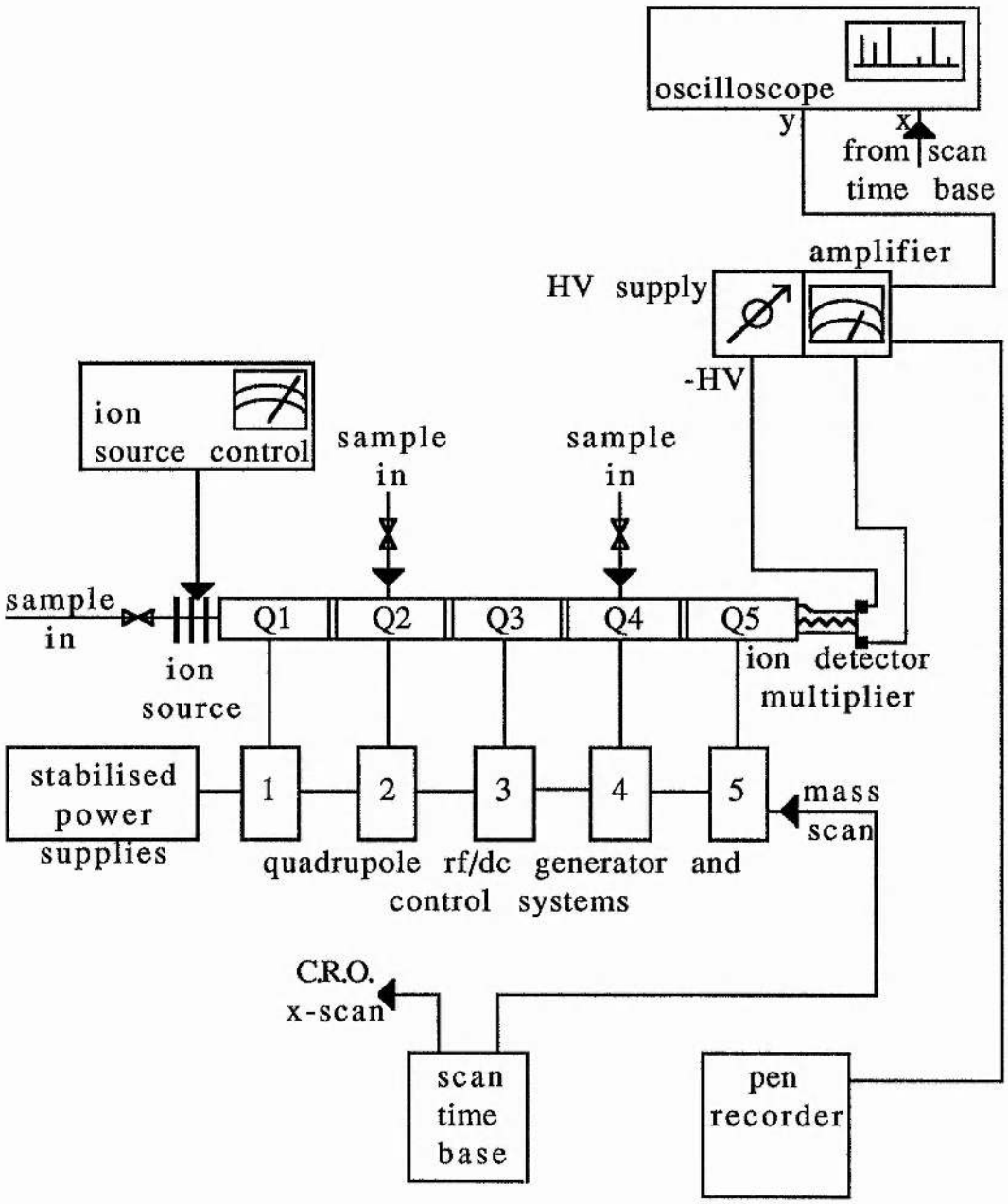
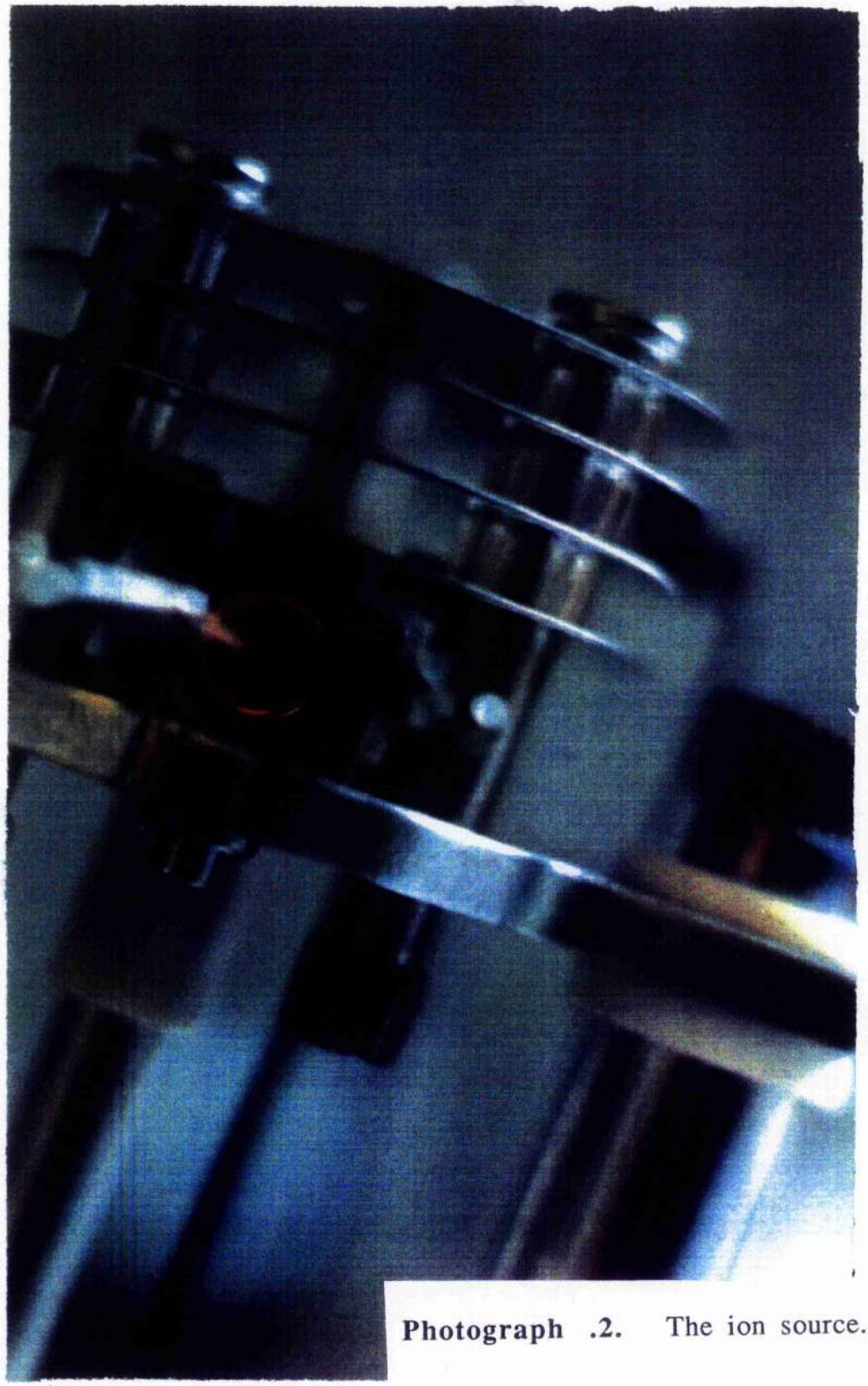


Figure 4.3. Schematic diagram of the quinquaquadrupole mass spectrometer



Photograph .2. The ion source.

4.3 The instrument.

The components of the quinquaquadrupole mass spectrometer are described in the following section.

4.30 The ion source.(photograph2)

The original design for the ion source came from Prof J.H. Leck from the university of Liverpool, (described in the thesis of A.E.Holme.)[101] The present ion source incorporates a number of design modifications which will also be described in this chapter. Figure 4.4 shows the basic design of the ion source.

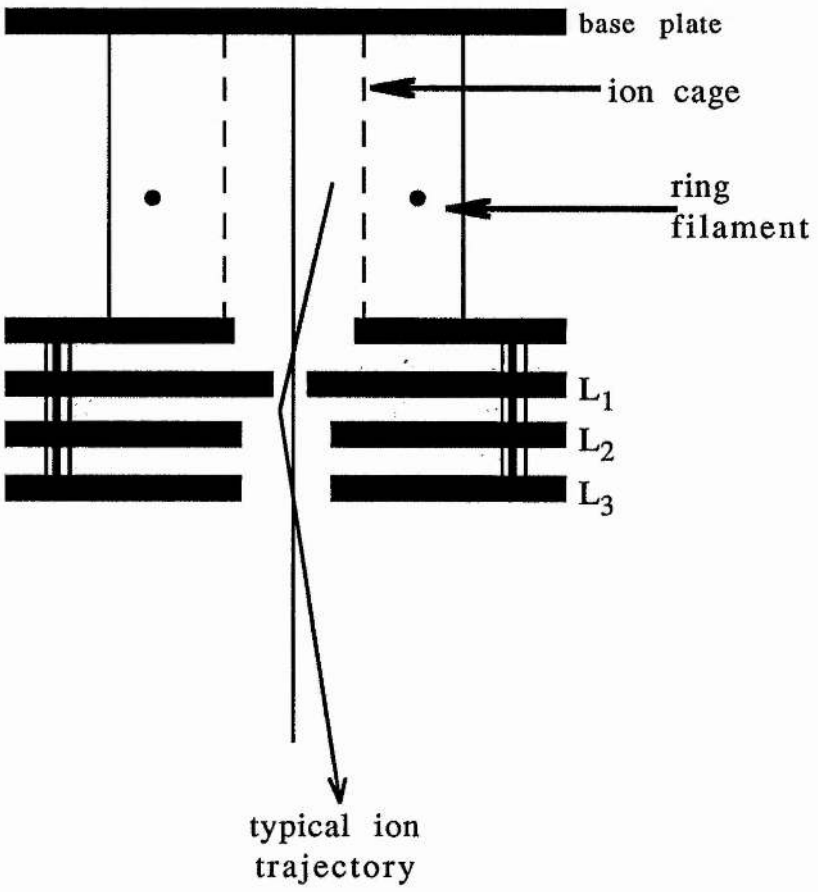


Figure4.4. diagram of the basic ion source.

The cage is made from 80% transmitting tungsten mesh on a 10 mm long stainless steel former and with an internal diameter of 7 mm. A ring shaped filament (10 mm diameter made of 0.150 mm thoriated tungsten) encircles the cage. There is a difference between the original design and our ion source in that the cage and filament are surrounded by a horseshoe shaped electron repeller which is connected to the negative leg of the filament. The ions generated in a particular fragmentation are attracted out of the cage area by the negative potentials on two focus plates situated 4mm from the cage. The focus plates are made of stainless steel and are circular being 44.35 mm in diameter and 2.0 mm thick. The plates have adjustable potentials. Focus one(L_1) can be varied from 0 to -150 volts and has an aperture of 1.5 mm while focus two(L_2) can be varied between 0 and -75 volts and has an aperture of 3.0 mm. There is a third plate which is earthed and has an aperture of 5.4 mm.

Throughout the initial stages of the quinquaquadrupole mass spectrometer development the focus plates behaved erratically. The solution to the problems with the focus plates was eventually discovered and will be described in this chapter.

4.31 Ion energy.

The ion energy control alters the cage potential relative to ground between 0 and +30 volts.

4.32 Electron energy

The electron energy is controlled by the potential between the cage and the filament from 20 to 75 volts. A typical operating value would be 40 volts. This serves to accelerate the electrons into the centre of the source.

4.33 The quadrupoles.

The quadrupole rods are 120 mm long and have a diameter of 6.0 mm. The spacing between each set of rods is 4.0 mm. The rods are shown in figure 4.5.

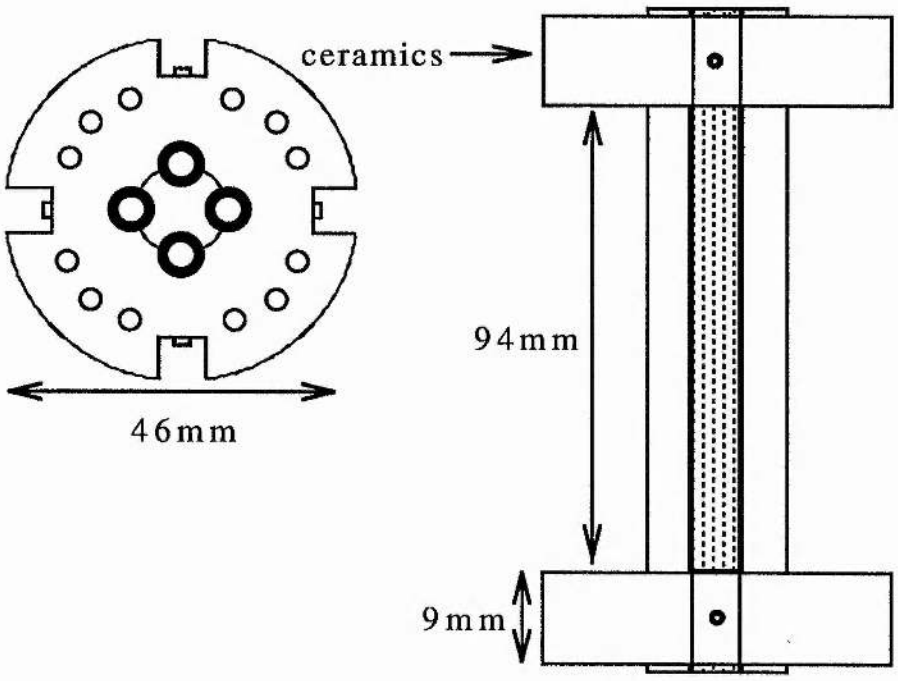


Figure 4.5 Diameter of the quadrupole rod system.

The rods operate as described in chapter one. The first set of rods were originally placed flush with the third focus plate. After investigation they are now approximately 2.0

mm from the third plate. The other sets of rods are embedded in a ceramic housing. There are no focus plates between the quadrupole rods. It was originally decided to exclude focus plates between the rods for two reasons. Firstly, even though the triple quadrupole mass spectrometer has focus plates between the rods it was found that they had little effect on the signal. Secondly, it was felt that the transmission of a signal from source to detector would be reduced if focus plates were introduced. In hindsight it may have been advantageous to include a certain number of focus plates between the quadrupole rods. However the number of plates and distance between them need to be carefully considered.

4.34 Pole bias.

The potential on each set of quadrupole rods can be altered relative to ground. The bias setting may be neutral, positive which serves to slow the ions down as they enter or negative which serves to accelerate the ions through the quadrupole. Theoretically the ideal pole bias settings should be as shown below.

QUADRUPOLE.	1	2	3	4	5
POLE BIAS.	-	+	-	+	-

The negative potential on the first set of rods should serve to pull the ions out of the source, the positive potential on the second quadrupole will slow the ions down and allow them to react with the neutral gas, the negative potential on the third quadrupole retards the ions and aids separation. Once selected an ion should pass into an area of positive pole bias on the fourth quadrupole and finally into a negative pole bias in the fifth. The pole bias settings on the quinquaqaudrupole operate in the same way as those on the triple quadrupole mass spectrometer. However with the quinquaquadrupole it was found that the settings had to be adjusted for each particular system and at each stage of reaction. It has also been noted that the biasing of the rods had a marked effect on the extent of a particular ion molecule reaction. This will be fully discussed in chapter 5.

4.35 The multiplier.

The multiplier is a AEM 2000 model, shown in figure 4.6

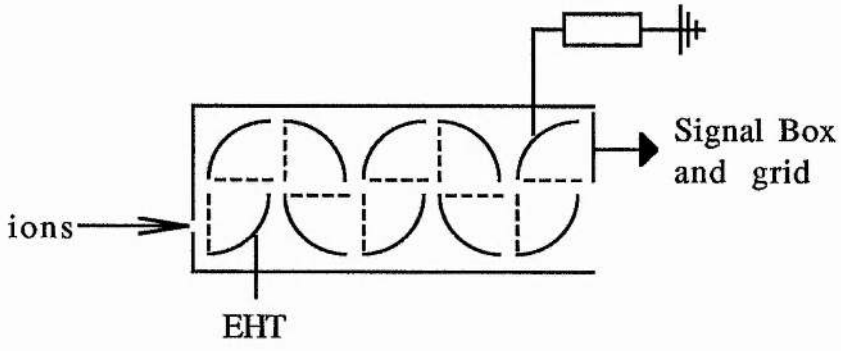


Figure 4.6. The electron multiplier.

This is a 17 stage high gain multiplier which incorporates an off axis first dynode to avoid photon radiation effects from the source filament. The multiplier dynode system is energised by a high voltage supply up to a maximum of 2.5kV. The current available from the multiplier output is amplified/converted to a direct voltage which is fed to an oscilloscope display for fast scan observation and a pen chart recorder for slow scan output.

The amplifier/converter has six switched ranges of input current producing a 10 volts output for an input current of 10^{-5}A to 10^{-10}A in decade steps. There is also a filter stage having switched response times from 10 ms to 3000 ms in six steps. This is useful for filtering noisy signals especially when scanning slowly.

4.36 Emission control.

The emission current was variable between 0 to 3mA. Throughout the initial stages of this work it was found that most of the controls behaved erratically. As the emission current was increased the ion current produced decreased. At certain times the maximum peak height was obtained with the emission current reading apparently zero. In fact when the emission current was checked using an external meter there was found to be a current of 15 Amps flowing

at emission zero. This is thought to be a result of the characteristics of the amplifier. This does not present a problem as most of the research was carried out with emission settings above 1mA. However the erratic behaviour of the signal did present a problem.

4.4 Instrumental developments

		For maximum peak height	
EMISSION	ION ENERGY	SIGNAL	L_2
	Volts	A	-
volts			
100	15	2.8 x10-9	-8.5
	20	2.o x10-8	-7.2
	25	2.8 x10-8	-3.5
	30	3.2 x10-8	-3.3
200	15	1.2 x10-9	-16.0
	20	1.4 x10-8	- 5.7
	25	5.0 x10-8	- 8.3
	30	6.8 x10-8	- 3.6
300	15	5.0 x10-10	- 7.9
	20	3.8 x10-9	- 24.0
	25	3.6 x10-8	- 10.5
	30	8.8 x10-8	- 9.6
400	15	*******	******
	20	1.2 x10-9	- 2.0
	25	1.2 x10-8	- 3.5
	30	1.2 x10-7	- 8.6
500	15	*******	******
	20	1.2 x10-9	- 2.8
	25	6.4 x10-9	- 2.9
	30	1.2 x10-8	-12.1

Table 4.1 Peak height variation with instrument settings.

Table 4.1 illustrates the kind of behaviour observed for an N_2^+ signal at a constant pressure setting over a range of

emission current settings, ion energy settings, electron energy settings. This type of behaviour made ion-molecule reaction studies impossible and attention was turned to solving this problem.

Numerous checks were made on the wiring of the ion source. Particular attention was given to the focus plates after consultation with Dr J Batey of V.G instruments, Dr D. Richards of Ledamass U.K, Professor J.H Leck of Liverpool university and the original designer of the ion source Dr A.E Holme, of Edwards vacuum systems. All the above mentioned people saw faulty wiring as the problem. However, despite extensive checks none of the wiring checks showed up any faults in the system.

Attention was then turned to the possibility of a charge build up of some sort between the focus plates. The ion source was removed and cleaned. It was found that the focus plates produce the maximum ion current when L_1 was at a high negative potential and L_2 is earthed. It was observed that the ion current, although large at these settings tended to decay over a 2-3 minute period, eventually falling to zero. The results seem to suggest that there is some interaction between L_1 and L_2.

It was decided to alter the position of the earth plate and the potentials on the remaining two focus plates. Periodically the plates were all set to 0 volts potential to remove any charge build up which might have been present. The results are shown in table 4.2.

	For maximum peak height.		
POSITIONING OF THE FOCUS PLATES	FOCUS$_1$ L_1 VOLTS	FOCUS$_2$ L_2 VOLTS	MAXIMUM ION CURRENT AMPS
L_1 L_2 E	–150	0	8.2×10^{-8}
L_1 E L_2	-150	-45	6.2×10^{-8}
E L_1 L_2	-150	-22	3.5×10^{-8}
L_2 L_1 E	-105	-35	3.5×10^{-8}
E L_1 E	-123	0	2.3×10^{-8}
L_1 L_1 L_1	-150	-150	4.2×10^{-8}
E E E	0	0	1.2×10^{-9}

Table 4.2. Variation in peak heights with alteration of the positioning of the earth plate and potentials on the other two plates.

Having studied these results it was decided to make it possible for the plates to have a positive potential. Having altered the source to achieve this another set of readings was obtained for the variation in peak height with potential on plates. The results indicated that only when the potential was positive on both L_1 and L_2 did a stable signal appear for longer than a few minutes. Even then this signal was very small, and therefore of no use. The results seem very strange as a positive potential is being applied to attract and focus a positive ion from the source.

The source was dismantled, washed using decon 90 and acetone, dried and returned to its mountings.

Settings for maximum peak height.

EMISSION	ION ENERGY	SIGNAL	L_2
microA	**volts**	**A**	**- V**
100	15	6.2×10^{-8}	- 29
	20	2.0×10^{-7}	- 24
	25	2.0×10^{-7}	- 16
	30	1.3×10^{-7}	- 20
200	15	6.0×10^{-8}	- 28
	20	5.4×10^{-7}	- 31
	25	1.0×10^{-6}	- 28
	30	1.4×10^{-6}	- 22
300	15	9.4×10^{-9}	- 20
	20	8.6×10^{-7}	-33
	25	1.5×10^{-6}	- 37
	30	2.7×10^{-6}	- 30
400	15	2.2×10^{-9}	- 14
	20	3.8×10^{-8}	- 24
	25	8.8×10^{-7}	- 34
	30	2.5×10^{-6}	- 35
500	15	1.2×10^{-9}	- 12
	20	8.4×10^{-9}	- 17
	25	3.8×10^{-7}	- 34
	30	2.0×10^{-8}	- 40

Pressure of N_2^+= 5×10^{-6}mbar. L_1= -100V

Table4.3 Peak height variation with instrumental setting.

It can be seen from the above results that there was a dramatic improvement in the signal height when the source was completely clean. Both emission and focus plates seemed to be functioning in the correct way. The tests shown in table4.3 were repeated approximately at 30 minute intervals and the results are shown in table 4.4 .

TIME MINS	L_1 VOLTS	L_2 VOLTS	ION CURRENT AMPS
0	–132	–47	8.6×10^{-8}
30	–123	–28	7.3×10^{-8}
60	-120	–29	8.3×10^{-8}
90	–138	–27	7.5×10^{-8}
120	–130	–20	7.3×10^{-8}

Pressure of $N_2^+ = 5 \times 10^{-6}$ mbar.

Table4.4 Variation in L1 and L2 for mavimum peak height.

After two hours the signal again became unpredictable and the focus plates returned to their original erratic behaviour. A further two hours later the signal was very small at all settings of emission and focus plates. The results again seemed to indicate that there was a build up of something on the source which caused the problem. It was decided to again remove the source and try to discover if material was present on the plates. The source was

removed and placed in a beaker of carbon tetrachloride for four hours.

The source was then removed from the beaker and the carbon tetrachloride was removed using a rotary evaporator. An infrared spectrum of the washings was recorded. The spectrum was found to be consistent with that of a hydrocarbon. The only possible explanation of the result is that either diffusion pump or rotary pump oil was contaminating the source. GC/MS spectra were recorded of the washings and of the pure diffusion and rotary pump oils. The results are shown in table 4.5.

m/e	WASHINGS FROM INSTRUMENT	DIFFUSION OIL(LR50)	ROTARY PUMP OIL
15.	*	*	
27.	*		*
41.	*	*	
53.	*	*	*
77.	*		*
85.	*		*
93.	*	*	
95.	*	*	*

n.b. Carbon tetrachloride peaks also present.

Table 4.5 GC/MS Identification of Washings from the Ion Source.

The results clearly confirmed the presence of both types of pump oil on the source. As a result of this finding the quinquaquadrupole mass spectrometer was completely dismantled.

4.40 Dismantling and reassembly of the quinquaquadrupole mass spectrometer.

Two modifications were decided upon to rectify the backstreaming of the pump oil. However, prior to this the whole instrument was dismantled, cleaned and reassembled. This proved a very time consuming task taking nearly two weeks. Upon examination it was found that the diffusion pump oil was cracked, and it was possible to detect pump oil on the entire apparatus. The quadrupole assembly was removed as one unit and washed with 40/60 petroleum ether.

The rods and source were then baked in an oven at 80°C for four hours. The original diffusion pump oil type Edwards Apiezion C was discarded and Santovac5 oil was used in its place. The advantages of this oil are shown in table 4.6.

OIL	TYPE	COST 500ml	VACUUM	VAPOUR PRESSURE
APIEZON C	HYDROCARBON	84.01.	3×10^{-7}	4.0×10^{-8}
SANTOVAC 5	POLYPHENYL ETHER	324.01.	3×10^{-10}	2.6×10^{-10}

Table 4.6 . Comparison between the available diffusion pump oils.

It can be seen from the above table that Santovac5 has a much lower vapour pressure and higher vacuums can be achieved when using it. Secondly two foreline traps (Edwards model f-l20k) were fitted between the diffusion and rotary pumps. The traps consist of baskets of alumina pellets and serve to catch any oil vapour backstreaming from the rotary pumps. An electronic cut out was wired into the system to ensure that should the cooling water stop flowing to the diffusion pumps the instrument would cut out automatically. This would minimize any rod contamination.

4.41 Instrumental performance with modifications.

Once again problems arose during the reassembly of the quinquaquadrupole mass spectrometer. Reinforced nylon tubes had been fitted between the rotary and diffusion pumps, and it was found that these tubes collapsed under

vacuum. In order to counter this, the tubes were removed and a steel spring inner was added to each of them. The filament burnt out upon switching on, and this had to be replaced before the work started.

Once completely reassembled, modified and pumped down to a pressure of $2x10^{-7}$ mbar a third study of the performance was carried out. Once again nitrogen was used as the primary ion source gas and the molecular ion was selected. The results indicated that the modifications had clearly improved the instrumental performance, the peak heights were much greater and the peaks were now stable.. The instrument attained pressures of $3x10^{-7}$ mbar without charging the baffles with liquid nitrogen. It was found that pressures of $1x10^{-7}$ mbar could be achieved on a cold day with the baffles fully charged with liquid nitrogen. As a result of this improvement in pressure the amount of primary ion source gas required to generate a good signal decreased markedly. The source could now be operated at $1x10^{-6}$ mbar. The advantages of lower pressure operation were that, quadrupole contamination could be minimized, pressure of the target gases could be increased and strain on the system could be minimized.

The results in table 4.7 show the instrumental performance over a number of days.

NO OF DAYS.	FOCUS L_1 VOLTS.	FOCUS L_2 VOLTS.	ION CURRENT AMPS.
1	–100	-30	8.8×10^{-8}
3	–122	-44	7.7×10^{-8}
5	–120	–43	6.2×10^{-8}
7	–132	-50	5.4×10^{-8}

Table.4.7 The behaviour of the focus plates over a period of seven days.

The results indicate that the performance of the instrument was deteriorating with time. A greater negative potential was required to produce a stable signal as time went on. It was observed that the focus plates again behaved erratically, giving no sharp focus. Another problem which was encountered at this stage was the gradual loss of emission upon introduction of primary ion source gas. There was a pronounced loss in resolving power of the first quadrupole, even at maximum resolution the signals from the first quadrupole could not be resolved. Each problem was studied in turn.

4.42 Erratic focus plate behaviour.

The initial reaction to this problem was that oil contamination was still occuring. The source was removed and the focus plates were studied very carefully, but no contamination could be observed. The plates were then analysed further using an electron microscope. All three focus plates were examined on both sides and at different points on each side, an elemental analysis was carried out on twelve parts of the plates. The trace showed no apparent contaminates on any part of the plates.

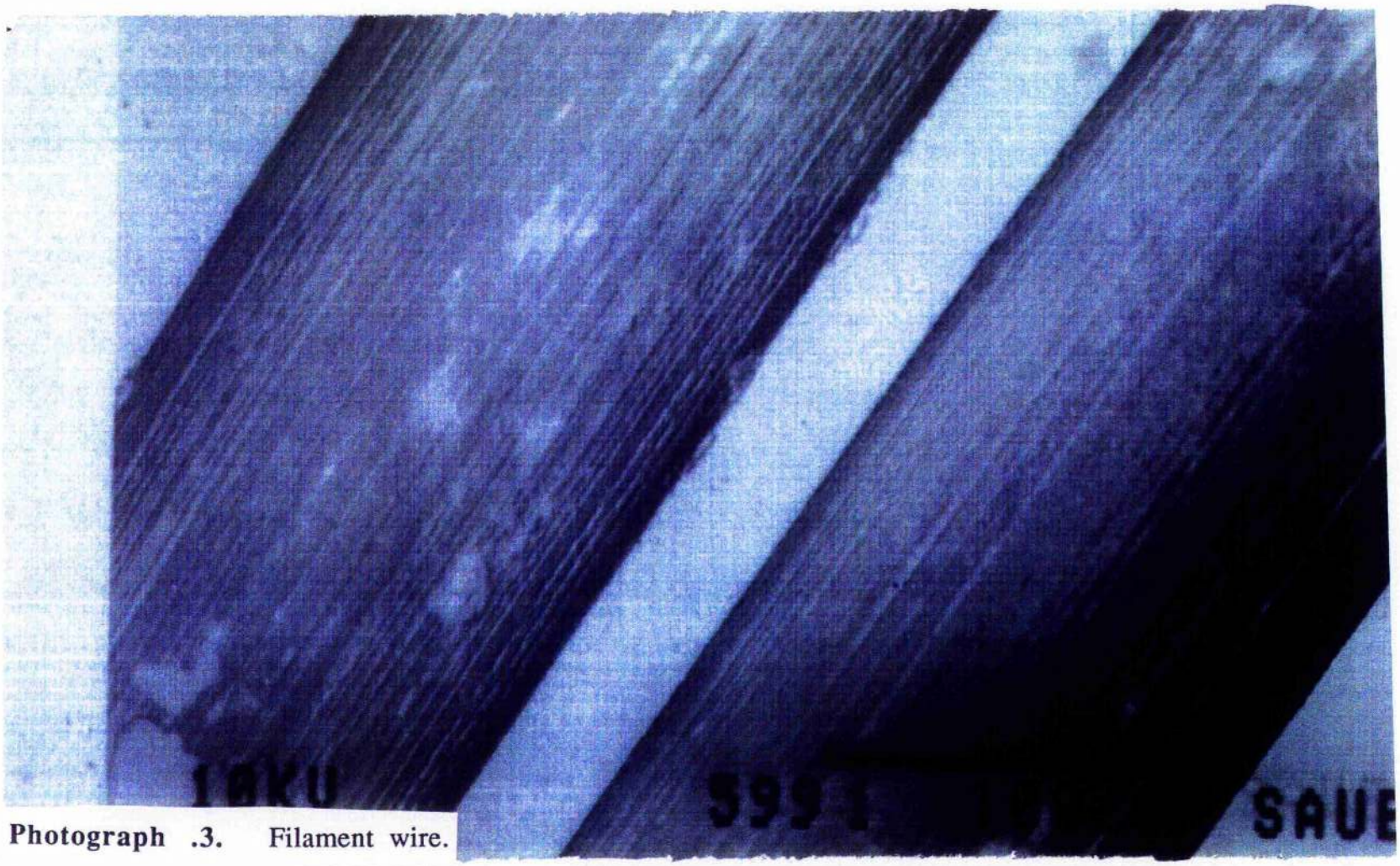
The plates were cleaned very thoroughly using a mixture of Decon90 and carbon tetrachloride and placed in a sonic bath for four hours

4.43 Loss of emission

It was felt that the loss of emission could possibly be due to abnormal behaviour of the filament. The filament wire used in the quinquaquadrupole mass spectrometer is made of thoriated tungsten, in the ratio 99.4% tungsten to 0.6% thorium. The presence of thorium as a monatomic layer on the surface of the tungsten enhances the electron emission up to twenty fold that of the pure tungsten wire. The thorium serves to reduce the work function of the tungsten allowing electrons to escape from the metal surface more efficiently. It was felt that the filament wire used could be deficient in thorium.

The filament was removed from the source and examined under an electron microscope. A new wire and an old wire were placed under the microscope and examined at six different places along their length. The results are shown in photograph3 .

It was discovered that the samples seem to have no trace of thorium in them. From the photo it can be seen that the old filament wire seems to be pitted as indicated by the arrow. The manufactures were consulted and they assured us that the wire had an even coating of thorium. Further tests were carried out on the wire using a using a second more powerful electron microscope instrument . The results indicated that there was indeed trace amounts of thorium in the wire however these were spread unevenly over a wide area of the surface. The signal from the thorium diminished with time. From the results it seemed clear that a new batch of filament wire should be used. It was found that the new filament responded far more uniformly than previously observed. Apart from the uneven distribution of the thorium on the tungsten surface two factors could be operating to cause the thoriated tungsten filaments to behave erratically. It is known that high operating temperatures of thoriated filaments cause evaporation of thorium from the surface of the tungsten. The rate of diffusion of the thorium to the surface of the wire may be too slow to replace the lost thorium and result in an uneven surface coating. This explains the pitting of the filament as



Photograph .3. Filament wire.

observed in photograph 3. Conversely if the operating temperature is too low insufficient thorium is released to cover the surface of the wire. Secondly thoriated tungsten wires can suffer damage by gaseous ion bombardment.

As a result of these investigations primary ion source pressures were kept to a minimum in order to limit the amount of ions present in the source, the filament current was kept at a lower level than had previously been used and the filament was changed at frequent intervals.

4.44 Erratic focus plate behaviour and poor resolving power.

The focus plates were removed and examined. Apart from the ion burns on the focus plates large ion burns were noted on the filament legs, the casing of the spectrometer and, upon close examination, on the ends of the rods of quadrupole one. Three modifications were made to the source. These were;

A. The third plate which originally had a 5 mm hole in it This was replaced with a plate with a 3 mm hole in it.

B. Two small metal plates(3.5 mm in length) were spot welded to the first plate.

C. Four small discs of P.T.F.E were cut and placed flush with the ends of the rods of the first quadrupole. It was hoped that these would stop any contamination of the rods by unfocussed ions emerging from the source and striking the rods.

The modified source is shown in figure 4.7

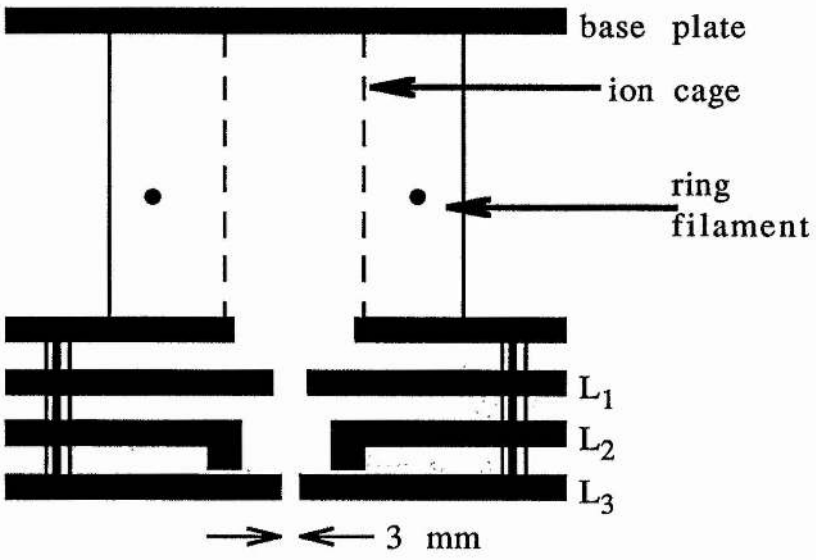


Figure 4.7. Modified ion source.

It was hoped that the smaller hole in the earth plate would cut down the amount of deposit on the focus plate. It is known that slight contamination on the rods causes large loss in the resolving power of the quadrupole . The two additional plates which were incorporated would in theory reduce the ion burns on the plates.

The source was reassembled and the instrument was pumped down. The resolving power of the first quadrupole was greatly improved. Peak splitting was not observed and the resolved peaks remained at a constant height for 3 days. It can be concluded that the original ion beam was unfocused as it left the original third plate. This resulted in the ion burns observed on the ends of the rods. This contamination of the rods destroyed the resolving power of the first quadrupole. Upon removal of the source after a period of 8 weeks it was noted that large ion burns were observed on the end of the third focus plate and no burns were observed on the ends of the rods. The third plate was acting as a shield.

The modifications had also improved the performance of the focus plates, and a consistent focus could now be obtained for both L_1 and L_2. It was also noted that the ion energy requirement became much smaller throughout the system. Ion energies of between 15 and 20 eV were required to complete a reaction sequence along the complete system. This aided the resolving power of the instrument as ions took relatively longer time intervals to travel through each quadrupole, and allowed studies of ion production as a function of ion energy to be made.

4.5 Further problems

The problems of a more chemical nature are discussed in chapter 5. Over a period of about four months more

instrumental problems became apparent. These will be discussed in turn:

4.50 Resolving power of the instrument.

The instrument was found to perform adequately for up to four weeks without any observable loss in resolving power. The time span was however dependent on the types of reagent gases used, the pressures of these gases and the amount of time the source was actually switched on. It was found that certain chemicals such as dimethyl ether, formaldehyde and some chlorinated hydrocarbons, when used as primary ion source gases, rapidly reduced the resolving power of the instrument. It was also observed that the instrumental performance was reduced if the source was left on after the experiment was completed or the gas pressures were kept high for any length of time. After two or three weeks it was found that resolving power of the first quadrupole was completely lost and after about four months it was found that the resolving power of quadrupoles three and five had also deteriorated appreciably. These observations seem to suggest that there is contamination of the rods by ions colliding with them. This is supported by the observed order in which the quadrupoles lose their resolving power. The first quadrupole is used as an ion filter and excludes all ions but the ion of

interest. There is consequently a large flux of ions on unstable trajectories hitting the rods of the first quadrupole. The third quadrupole also acts as a mass filter; however there are comparatively less ions to filter, and hence the rods remain uncontaminated for longer periods of time. A similar situation exists at the fifth quadrupole. It was also noted that the range over which the spectrum was resolvable decreased with time. Initially a mass scan of approximately 80 mass units could be obtained with good resolution. Over the four month period the resolvable scan range decreased to about 30 mass units. The upper and lower ends of the scan were poorly resolved and only the middle section was clearly defined. After long periods of use at high pressures it was observed that upon pumping the gases out the resolution on the first quadrupole failed to return. A very large unresolvable peak remained for up to 15 hours. It was initially thought that the disc previously inserted to create a greater pressure differential between the source and the quadrupoles was hindering the pumping of the instrument as a whole. In order to establish if this was indeed the fault the disc was removed and methane was passed into the source at a pressure of 8×10^{-5} mbar. The inlet valve was then closed and the system was allowed to pump. Spectra were recorded at 5 min intervals The results showed that the disc was reducing the pumping efficiency. The size of the unresolvable peak was reduced after only a few minutes, however the pressure differential

between quadrupoles was also decreased. The second and third penning gauges rose as the methane was passed into the ion source. However the problem of loss of resolution after an experiment continued, and clearly there was still something fundamentally wrong in the source/focussing set up. It was decided to investigate methods by which the transmission, resolution and focussing of the instrument could be improved.

4.6 Further modifications to improve the source and quadrupole performance.

4.60 Introduction.

A complete search of the literature revealed three possible methods by which the performance of the source and first quadrupole might possibly be improved. The first was the introduction of a prefocussing quadrupole between the source and the first quadrupole. A device known as a Brubaker lens has previously been reported [102] .

A modification such as this was considered carefully. There were a number of problems associated with the introduction of a 'sixth mini quadrupole'. A separate rf generator would have to be constructed . Also it has been previously noted that the connections to the quadrupole rods interfere with one another and it would have been difficult to introduce the connections to the prefilter without

causing even more interference. It was also very unclear as to the required accuracy of alignment and lengths of the rods.

A second possibility was to introduce a device known as a bunching box.

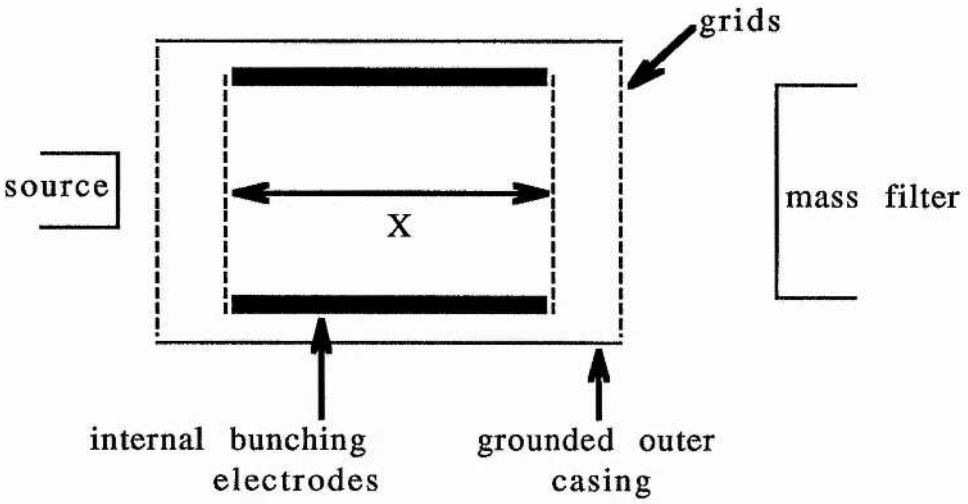


Figure 4.8 Schematic representation of a bunching box

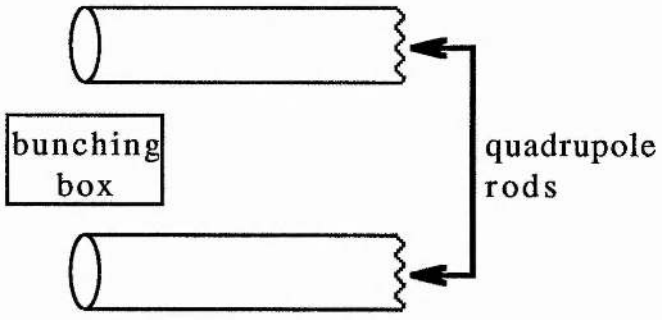


Figure4.9 Positioning of the bunching box between the quadrupole rods.

This device was first described by Lefaivre and Marmet[103]. As the name implies the ions are bunched and injected at the proper phase into the first quadrupole. A diagram of the bunching box is shown in figures 4.8 and 4.9. It was decided not to pursue this possibility as it would again require a significant amount of modification to the electronics of the instrument.

The third option was to introduce a tube made from a leaky dielectric material between the source and the first quadrupole. This type of approach was first examined by Fite[104] to reduce the effect of fringing fields on a quadrupole mass spectrometer. The tube behaves as a conductor towards dc and a dielectric towards the rf field. This effectively eliminates the dc component from the field at the entrance to the quadrupole. There is no information as to what particular composition of ferrite material would be most suitable for application to our particular set up, however, Fites' investigations were carried out using nickel/zinc composite ferrites. One advantage of this approach was that only an earth connection is required to the tube, and this can be made easily via the last focus plate on the source. It was decided to investigate the use of ferrite tubes further.

4.61 Studies of ferrite rods as quadrupole prefilters.

Introduction.

With the existing set up the introduction of the ferrite tube required that considerable modifications be made to the source set up. Moving the source completely back to the base plate gave an upper limit of 50 mm to the length of the tube. As the tube was to actually fit inside the rods of the first quadrupole then the outer diameter of the tube was fixed to a maximum of 5.53 mm. However nothing could be predicted about the performance of any one tube, it was unclear as to how the bore, length, overall diameter and composition of each ferrite would effect the performance of the ion source and first quadrupole. A secondary problem involved the existing focus plates. It was unclear as to the requirements of the source plates in terms of hole size, number of plates and order of plates.

4.62 Initial investigations

The following ferrite tubes shown in table 4.8 were obtained from Neosid limited, a specialist manufacturer of ferrites.

Ferrite	Length	Outer Diameter	Inner Diameter	Ferrite Type
	mm	mm	mm	
F 8	38	4	1.5	Magnesium/Zinc
F 8	35	4	2	Magnesium/Zinc
F 14	25	4	1.5	Nickel/Zinc
F 14	20	4	2	Nickel/Zinc

Table4.8. Types of ferrite tubing obtained.

After numerous attempts to centre the tube by attaching it directly to the earthed focusing plate it was decided to construct a holder as shown in figure 4,9.

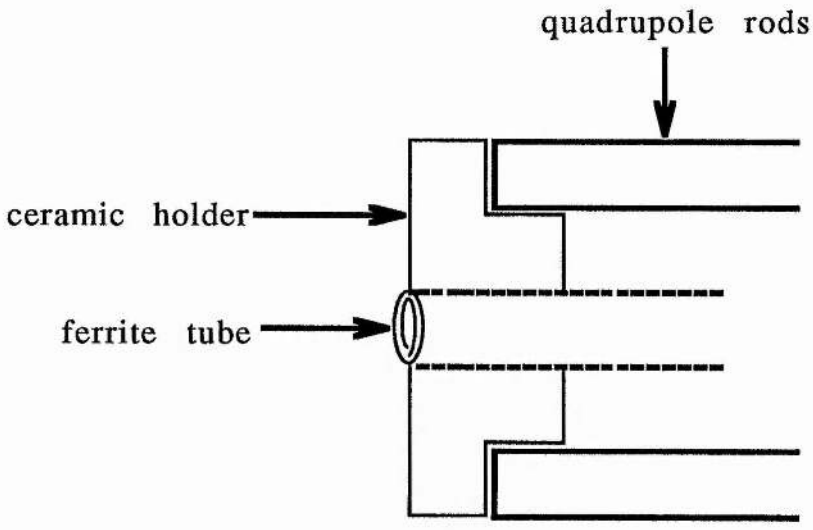


Figure4.10. Ferrite tube holder.

The ceramic was precisely machined to the diameter of the inscribed hole made by the quadrupole rods. The earth connection to the ferrite was made via the last lens plate. In

order to reduce the amount of adjustment required throughout this investigation it was decided to start with the tube of smallest diameter and work upwards. Ferrite tubes of varying inner and outer diameter, varying dielectric constant and varying length were used in the investigations. Testing the properties of each of the tubes involved considerable time because the instrument had to be taken down to atmosphere, dismantled, cleaned and reassembled each time a new tube was tested. The tuning of the first quadrupole also had to be adjusted after the insertion of each new ferrite tube. After an initial study of the available tubes it was decided that although the variation in performance between the different sizes and composites ferrite tubes was not marked(table4.9), the wide bore nickel zinc ferrite should be studied further. It seemed to retain its stable peak height longer than the other ferrites

Ferrite	Inner Diameter mm	Maximum stable ion current/A (10 mins)	Maximumstable ion current/A (30 min)
F 8	1.5	5.2×10^{-7}	1.4×10^{-9}
F 8	2.0	9.3×10^{-7}	1.6×10^{-7}
F 14	1.5	7.8×10^{-6}	9.6×10^{-7}
F 14	2.0	7.1×10^{-7}	5.9×10^{-7}

Nitrogen pressure= 1×10^{-6} mbar.

Maximum ion current with no ferrite tube present= 7.2×10^{-8} A.

Table4.9. Maximum current achieved using different ferrites as prefocussing tubes.

A further three ferrites of differing overall length were prepared and tested; the results are shown in table 4.10.

Ferrite	Inner Diameter mm	Length mm	Maximum stable ion current/A (30 min)
F 14	2.0	20	4.2×10^{-6}
F 14	2.0	15	1.8×10^{-6}
F 14	2.0	10	3.7×10^{-7}
F 14	2.0	5	1.9×10^{-7}

Nitrogen pressure = 1×10^{-6} mbar.

Maximum stable ion current without the ferrite = 8.5×10^{-8} A .

Table 4.10 Performance of the F14 ferite.

Clearly there is an improvement the ion transmission when incorporating a ferrite tube between the last lens plate and the first quadrupole. However this was by no means constant. After a period of time the effect diminished noticeably. Possible explanations for this are:

A. The temperature in the source area has an effect on the performance of the ferrite, reducing its dielectric properties.

B. The actual heating effect of the rf fields could be destroying the dielectric properties of the ferrite.

C. The bombardment of the ferrite with ions could in some way reduce the dielectric properties of the ferrite

Using ferrite tubes as quadrupole prefocussing devices for the quinquaquadrupole mass spectrometer does seem to have some potential. There are many ferrites available and the number of variables in our particular system is large. It was decided to operate the instrument without any prefocussing device for the present time. Different compositions of ferrite tubes, differing in overall length, outer diameter, inner diameter and at a different distance from the source may have improved the transmission and resolution of ions, and this is perhaps something to investigate in the future.

4.7 Further problems with the pumping of the quinquadrupole mass spectrometer.

The pumping of the quinquaquadrupole mass spectrometer had previously received some attention(see sec 4.40). There were however still problems with the system. They became particularly apparent when the instrument was subject to pressures around 1×10^{-4} mbar. It was noted that after an experiment the pumping was apparently very efficient, as indicated by the pressure readings on the penning gauges. However upon examination of the background spectra from

the first quadrupole it was found that very large unresolvable clusters of peaks still occurred. These peaks remained for anywhere between a few hours and days. A number of possible causes of this problem were examined in turn.

4.70. Contamination of the diffusion pump oil.

In order to investigate any possible Santovac5 contamination at the source end, the instrument was dismantled and the small diffusion pump was removed. Visual inspection of the oil showed no apparent difference between the used sample and a new sample. Both samples were sent for analysis. The GC/MS of the old and new samples were almost identical. The pump was thoroughly cleaned, given a fresh charge of oil and the instrument was reassembled. No apparent improvement was observed.

4.71 Reduction in pumping efficiency due to contamination of the foreline traps.

The alumina baskets in the foreline traps were removed and examined. Both samples of alumina were found to be discoloured by rotary pump oil. It was felt that the alumina might also be contaminated with some of the waste gases. The foreline traps were charged with fresh samples of alumina and argon was allowed into the system. No

apparent improvement was observed in the peak resolution and pumping. Charging of the foreline traps with fresh alumina samples was carried out every month.

4.72. The trapping of waste gases on the inner surfaces of the nitrogen traps.

It was felt that there may be some interaction between the oil deposits on the inner surface of the nitrogen traps and the exhaust gases.

To examine this the system was filled with neon to a pressure of $1x10^{-4}$mbar and then pumped down. Neon will not condense onto the inner surfaces of the traps. It was noted that the neon was pumped away a factor ten times quicker than other gases. This observation seems to reinforce the theory that the waste gases are lingering on the surfaces of the traps.

4.73. Nitrogen traps.

From the results obtained so far it seemed almost certain that some contamination of the system was occurring with time. It was decided to investigate the possibility of rod or source contamination with minute amounts of the diffusion pump oil.

Previously it had been noted that the performance of the first quadrupole had always been far inferior to the other

four quadrupoles. The source and first quadrupole system is pumped by an Edwards EO4 diffusion pump, and this pump is much smaller than the Edwards EO3 diffusion pumps which pump the rest of the system. It was felt that perhaps the diffusion pump oil from the EO4 pump was cycling up into the system and coating the source and first quadrupole. It seems reasonable to suggest that because the distance the oil travel can travel before entering the system in the larger pumps is much greater, therefore problem of oil drifting into the system from these pumps is much less. It was decided to dismantle the system completely and to clean it thoroughly and attempt to keep the liquid nitrogen traps filled at all times. Over a period of two weeks the system was completely dismantled. The rod system was soaked for three days in a bath of 40/60 petrol and then baked at $60^{o}C$ to $70^{o}C$ in an oven. The ion source was removed and dismantled, the cage was replaced with new wire mesh and the complete source system was scrubbed and baked in an oven between $60^{o}C$ and $70^{o}C$. The casing was meticulously scrubbed with petrol and dried with two lamp units. This avoided the use of blow driers which might have contaminated the system with dust. The instrument was reassembled, the liquid nitrogen traps were filled and the pumps were switched on. The traps were topped up at 2 hour periods and at no time were they allowed to drop below three quarters full. The laboratory was kept cold to reduce the loss of the liquid nitrogen.

4.74 Results.

A pressure of $1X10^{-7}$mbar was attained after approximately 30 hours pumping. Throughout the next 24 hours spectra of the background were recorded it was noted that all spectra were completely resolved. It was also noted that the size of the peaks varied considerably from quadrupole to quadrupole.

During the fourth day a tube carrying liquid nitrogen split. Liquid nitrogen poured onto a plastic tube under tension at a pressure of $1X10^{-7}$mbar. The tube fractured bringing the whole instrument instantaneously to atmospheric pressure resulting in diffusion pump oil being sprayed throughout the entire machine. Although the problem was quickly discovered and the pumps were switched off, it was too late to avoid not only complete contamination of the system, but also the rupturing of the main vacuum seals between the diffusion stacks and the cold traps. Once again a major overhaul was required.

4.75 Modifications, Dismantle and reassembly.

In order to minimize the possibility of pipes fracturing in the future the following modifications were introduced;

A. The liquid nitrogen traps were turned through 180^{o}. Any leakage from them would now flow away from the plastic piping.

B. A board was placed between the traps and the rotary pumps. Any leakages would now flow onto the board.

C. The amount of plastic tubing was reduced and the remainder rerouted to minimize the tension in the pipe work.

The rod assembly source and multiplier were completely dismantled and the diffusion pumps were removed. The pumps were cleaned with dichloromethane and baked in an oven at 80^0 C. The rods and source were carefully wiped with dichloromethane and then soaked in petrol 60/80 for three days. The rod and source assembly were baked at 60^0 C for 48 hours.The casing of the instrument was cleaned thoroughly using first dichloromethane and then petrol. Light bulbs (100 watt) were placed along the inside of the casing and left on for 3 days. The instrument was reassembled and allowed to pump down keeping the cold traps filled with liquid nitrogen at all times. A typical well resolved spectrum is shown in photograph 4.

4.76 Instrumental modification.

One of the major problems encountered in running the quinquaquadrupole mass spectrometer was the high pressure required to produce a significant reaction in the fourth quadrupole. The high pressure causes a loss in

resolution in the fifth quadrupole. The casing holding the quadrupoles and ceramics in place has a number of holes in it to improve the pumping. It was felt that as the pumping of the instrument had been significantly improved some of these holes might be covered up thus improving the efficiency of the ion molecule reactions occurring in the fourth quadrupole and reducing the overall pressure of gas required in the system. A steel sleeve was carefully fitted around the casing of the fourth quadrupole covering up the holes. To test the effect of this modification Ne^+ was generated in the source and selected in the third quadrupole. Nitrogen was passed into the fourth quadrupole and the charge exchange reaction was recorded in the fifth. The pressure of nitrogen to produce the same ion current of N_2^+ with the sleeve in place was 8×10^{-6} mbar. This compared to a nitrogen pressure of 5×10^{-5} mbar without the sleeve. The sleeve was retained for all further investigations as it had reduced the amount of target gas required to produce a workable signal in the fifth quadrupole. A similar sleeve was also fitted to the second quadrupole and was also found to reduce the amount of target gas required to produce a significant ion current for an ion molecule reaction in the first three quadrupoles.

4.8 Further pumping modification.

4.80 Introduction

Throughout the development of the quinquaquadruopole mass spectrometer the efficiency of the differential pumping had been questioned. It had always been observed that the readings from all three penning heads altered to some extent when a primary ion source gas or a target gas was introduced into the system. It was decided to investigate this problem with a view to improving the pumping differential throughout the system. A simple experiment illustrated the extent of the problem. Dimethyl ether was introduced as the primary ion source. This produced fragment peaks at m/e 45, 46, 29, 15, 31, 45. The peak at m/e 29 corresponding to the CHO^+ ion was selected and passed through to the third quadrupole . The primary ion source gas was removed and dimethyl ether was emited as a target gas into the second quadrupole. It was noted that as the pressure of target dimethyl ether was increased the peak corresponding to m/e 29 reappeared. This indicated that target gas is leaking into the ion source. In an attempt to eliminate this problem two modifications were made;

A. The baffle disc spacing (two dics with a hole in each of them situated between the nitrogen traps and the main pumping system) was increased to increase the efficiency of pumping of each diffusion pump.

B Polytetrafluoroethylene (P.T.F.E) discs were shaped and placed between the source and quadrupole one and quadrupoles three and four.

It was felt that a more efficient separation system would lead to less gas being required to produce observable peak heights. The introduction of less gas leads to greater resolution throughout the system.

4.81 RESULTS.

The introduction of a P.T.F.E disc between the source and the first quadrupole resulted in a much better separation of primary ion source gas and the first target gas. This in turn improved both the primary ion production and ion molecule reaction relative to the amount of gas introduced .

The introduction of the second P.T.F.E disc between the third and fourth quadrupole caused the entire pumping system to be thrown out of balance. Primary ion source gas mixed with first target gas and the first and second target gases mixed together. The disc was repositioned a further 10cm away from the first disc. The reasoning behind this was as follows.

The initial positioning of the second disc caused the first target gas to be confined into a volume of approximately 1100 cm^3. This may have resulted in too great an initial pressure for the first disc to cope with upon introduction of target gas into the second quadrupole. The gas flow into the source area would reduce the pressure of target gas in the confined space, and this would in turn lead to flow of the second target gas into the first target gas chamber. Moving the second disc back a further 10 cm would increase the allowed volume for the first target gas and, it was felt, produce a more balanced pumping system.

The modification resulted in a re-establishment of the pressure differential between the source and the quadrupole system and introduced a smaller differential between the 1st, 2nd and 3rd quadrupoles and the 4th and 5th. An experiment was carried out with the disc in this position and the results are shown in table 4.11. The instrument was once again dismantled and the disc was repositioned a further 6 cm away.

KEY:

A= No disc

B= 16 cm from first disc.

C= 24 cm from first disc.

D= 30 cm from first disc.

E= 38 cm from first disc.

P.T.F.E SET UP	PRESSURE OF NITROGEN REQUIRED mbar	ION CURRENT AMPS	PRESSURE DIFFERENTIAL BETWEEN SOURCE AND QUAD 1.
A.	1×10^{-6}	8×10^{-8}	NONE
B.	8×10^{-7}	8×10^{-8}	SOURCE 5.5×10^{-6} SYSTEM 3.4×10^{-7}
C.	8×10^{-7}	8×10^{-8}	SOURCE 1.2×10^{-6} SYSTEM 3.5×10^{-7}
D.	5×10^{-7}	8×10^{-8}	SOURCE 2.4×10^{-6} SYSTEM 6×10^{-7}
E	5×10^{-7}	8×10^{-8}	SOURCE 4.2×10^{-6} SYSTEM 9.1×10^{-7}

Table 4.11

The positioning of the disc seems to have a marked effect on the establishment of pressure differentials between the chambers which in turn affects the efficiency of reaction and resolution.

From the results obtained it seemed likely that the optimum position for the disc falls somewhere between 16 and 24cm away from the inlet to the second quadrupole. It was decided that the disc should be repositioned 16cm from the second inlet.

Optimum positioning of the disc may not have been fully established, however due to the amount of time required for each test it was decided to operate the machine without any further investigation into disc positioning.

4.82 Modifications to the gas inlet valves.

In an attempt to increase the number of target gas molecules in quadrupoles two and four for a given pressure a modification was made to the diameters of the outlet apertures on each valve. The original outlets had diameters of 7.11mm and only a small amount of the target gas would actually be getting in between the quadrupoles. The target gas would probably have collided with the rods and flowed into the area between the rods and the casing.

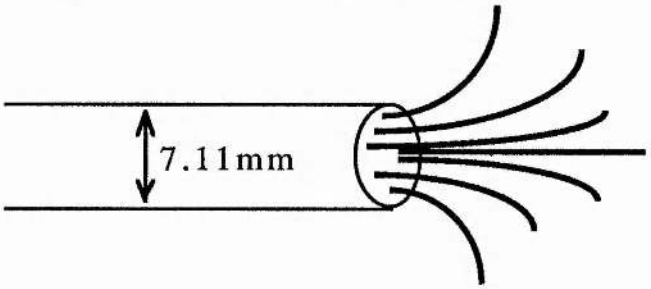


Figure4.11 Gas inlet to quadrupoles (unmodified)

This is clearly unsatisfactory as much of the target gas flows outside the reaction area. The diameter of the outlet apertures were reduced to 1.55mm.

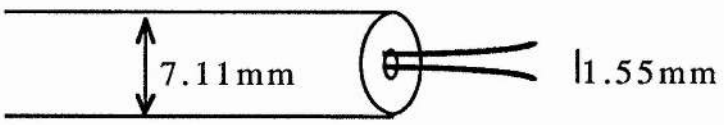


Figure 4.12. Modified gas inlet.

Identical reactions were carried out before and after this modification. Before the modification a pressure of $4x10^{-6}$ mbar of methane was required to produce an ion current of $6x10^{-7}$A for the CH_4^+ ion when charge exchange occurred with the Ne^+ ion in the second quadrupole. This pressure was reduced to $9x10^{-7}$ mbar to produce the same signal with the modification. This improvement was also observed between the third and the fifth quadrupoles,

It has been shown that with the inlet modification a much lower pressure of target gas produces the same amount of reaction. This must be due to the improved directing of the target gas into the reaction chamber. Attempts could have been made to study the effect of altering the outlet diameter on the extent of reaction, however due to the time constraints it was decided to operate the instrument with 1.55mm outlets.

It must be stressed that although significant progress has been made into the improvement of the pumping system it still remains the most inadequate area of the quinquaquadrupole mass spectrometer. Although a significant degree of pressure differential has been achieved between the various reaction chambers there is clearly some scope for improvement. This is apparent when the outlets between the casing and the diffusion pumps are cooled with dry ice while conducting an experiment. Cooling the source and first outlet improves the pressure differential between the system and the fourth and fifth qaudrupole. This effect

is probably due to the flow of gas back from the fourth quadrupole to the area of lower pressure,i.e. the third and second quadrupole.

A set up had now been achieved whereby a significant pressure differential could be obtained between the ion source and the first second and third quadrupoles and a smaller pressure differential could be obtained between quadrupoles one, two and three and quadrupoles 4 and 5. Certain disadvantages still remained with this set up. The major problem was the amount of time required to expel the gases at the end of an experiment. There has to be a compromise situation reached between the amount of target gas required and the time taken to pump the system. Sometimes as much as 2 hours were required to expel gases, particularly chlorocarbons. Pressures were kept as low as possible throughout all investigations in order to minimize this problem.

4.9 Summary.

A stage in the development of the quinquaquadrupole mass spectrometer had now been reached were ion molecule reactions could be followed through all five stages of the instrument. The production of ions in the source had been improved to a point were only a small amount of primary ion source gas was required to produce a primary ion signal capable of being transmitted along the entire length of the instrument. The reduction in the amount of primary ion source gas in the source chamber reduced contamination of the focus plates and thus increased the time between each overhaul of the source. The operation of the instrument at reduced source gas pressures minimizes the possibility of spurious results due to filament damage. The amount of target gases required to produce significant ion molecule reactions in the second and the fourth quadrupoles has also been minimized. This not only reduced the rod contamination, but also the reduced pressures give rise to much improved resolution. All quadrupoles acting as mass analysers are now capable of good resolution over a mass range of 15 to 90 m/e.

The introduction of foreline traps, Santovac 5 and a high quality rotary pump oil into the pumping system has produced a marked improvement in the pumping of the instrument. Initial pressures of 1×10^{-7}mbar can now be obtained. Providing the nitrogen traps are always full when

the diffusion pumps are on, contamination of the rods with oil can be almost eliminated. The foreline traps have reduced the contamination of the instrument by backstreaming from the rotary pumps to a minimum. The introduction of physical barriers at points in the instrument have resulted in significant improvements in the separation of the various gases. This has in turn has improved the amount of reaction obtained for a given amount of target gas and reduced the overall amounts of gases required in the system. Again reduced amounts of gases result in improved ion transmission and quadrupole resolution.

A decision was made to operate the instrument in its present state. It seems clear that major improvements in the instrument are still possible and these will be discussed in section 4.9 . However the financial and time constraints have limited any further instrumental modifications at this stage.

4.90 Suggestions for further improvements and modifications to the quinquaquadrupole mass spectrometer.

From the developments to date it can clearly be seen that there is a considerable scope for further improvements to the instrument. The principle areas where these could be carried out will be considered in turn.

4.91 Pumping.

The pumping of the system has caused considerable problems throughout the development of the instrument. The actual pressures reached are satisfactory. However the differential between the individual quadrupoles is still far from ideal. The introduction of turbomolecular pumps in place of the present diffusion pumps, although costly, would undoubtedly reduce the pumping problems. It is likely that a significant improvement in the pumping of the system could then be achieved by incorporating partitions between the individual quadrupole units. The present pumping system could be improved by the introduction of a valve system between the main quadrupole chamber and the diffusion pumps. This would allow the system to be sealed under vacuum while the liquid nitrogen traps were not filled. The diffusion pumps could then be left on when the instument was not in use. Another useful facility would be the introduction of a thermostat to control the temperature that each diffusion stack reaches. This would enable the diffusion pump oil to be warmed while the instrument is not in use, thus consideably reducing setup time. Finally the introduction of an automated filling system for the liquid nitrogen traps must be incorporated into the instrumental design.

4.92 Ion Source.

The ion source in its present state of development is operating satisfactorily. However the beam focussing system needs further improvements. It is felt that the source could be made more efficient by further investigation into the spacings of lens plates, aperture sizes and the potentials applied to the lens plates. The construction of a piece of apparatus to test the source and allow optimization externally would greatly reduce the time required to assess any modifications.

4.93 Quadrupole system

The major improvement which should be considered is the introduction of lens plates between each set of rods. Originally lens plates were omitted from the system because they served little purpose in the triple quadrupole mass spectrometer. It was also felt that they would reduce the ion beam and make detection difficult. It is clear that this was a mistake and lens plates should now be fitted between each set of rods. The number, potential on each, spacing and apature size would all need investigation.

The next chapter includes the results obtained from investigations into the instrumental parameters of the

instrument at this stage of development and also the results of ion molecule reaction studies undertaken.

Chapter five.

Chemical and physical investigations undertaken using the quinquaquadrupole mass spectrometer.

5.CHEMICAL INVESTIGATIONS ON QUINQUADRUPOLE MASS SPECTROMETER.

5.10 Experimental.

The operation of the quinquadrupole mass spectrometer is, in principle the same as that of the triple quadrupole mass spectrometer described in chapter 2. A vacuum line is attached to the instrument to allow the introduction of gaseous samples. All sample gases were introduced using the same experimental precautions described in Chapter 2. When the instrument was in operation the three liquid nitrogen traps were always kept topped up to avoid oil backstreaming into the system. The source was dismantled at monthly intervals and cleaned thoroughly.

5.11.Introduction.

In the early stages of experimental work the quinquaquadrupole mass spectrometer was used as a triple quadrupole mass spectrometer. It was felt that a greater understanding of the optimum settings for operation could be gained by using a combination of the first quadrupole and either quadrupoles two and three or three and five. Initial experiments were undertaken to optimize ion beam transmission, resolution and to gain an understanding of the performance parameters

5.2 Physical experiments.

The following physical experiments were undertaken to examine the overall performance of the instrument in its present state of development:

A. Determination of the variation in peak height with varying emission current settings.

B. Determination of the variation in peak height with varying electron energy settings.

C. Determination of the variation in peak height and resolution with varying ion energy settings.

D. Determination of the variation in peak height and resolution with varying focus plate potentials.

E. Determination of the variation in peak heights and resolution with varying settings of the pole bias.

5.20 Emission current settings verses peak height.

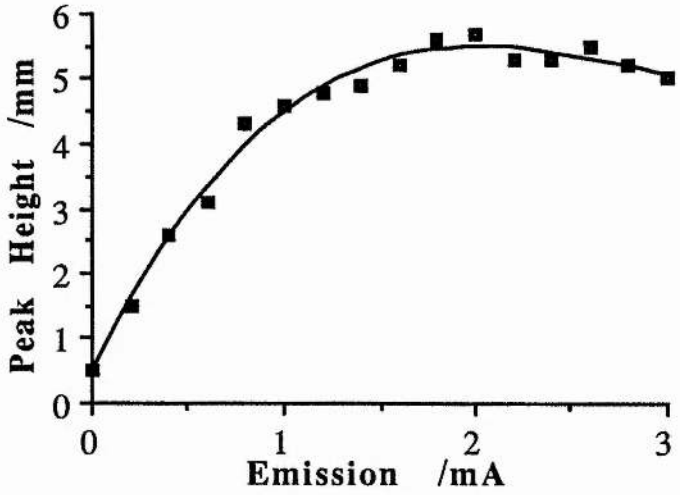
A sample of nitrogen was introduced into the mass spectrometer at a pressure of 1×10^{-6}mbar. The first quadrupole was tuned to mass 28 corresponding to the N_2^+ ion and the other instrumental perameters were optimized to give the maximum signal. The emission current was then varied from zero to 3.0mA and the peak height recorded. A

second set of peak heights were recorded while varying the emission current from 3.0mA to zero. An average of the two readings was taken in order to minimize errors due to pressure fluctuations or power surges. The results are shown in table 5.1.

EMISSON	PEAK HEIGHT	EMISSON	PEAK HEIGHT
mA	mm	Volts	mm
0	0.5	**1.8**	5.6
0.2	1.5	**2.0**	5.7
0.4	2.6	**2.2**	5.3
0.6	3.1	**2.4**	5.3
0.8	4.3	**2.6**	5.5
1.0	4.6	**2.8**	5.2
1.2	4.8	**3.0**	5.0
1.4	4.9		
1.6	5.2		

Table. 5.1 Relationship between peak heights and emission settings.

The above results are also depicted in graph 5.1.



Graph 5.1. The relationship between emission setting and peak height.

The peak height varies as one would predict. The peak height increases gradually as the emission current is increased from 0 to 2mA. After this there is no real increase in peak height up to the 3mA maximum.

This indicates that the source is operating at its maximum efficiency at around 2mA. As previously described the instrument should be operated at low emission current settings to prolong the lifetime of the filament. However each time the source was removed for cleaning the filament was replaced to ensure as uniform operation as possible.

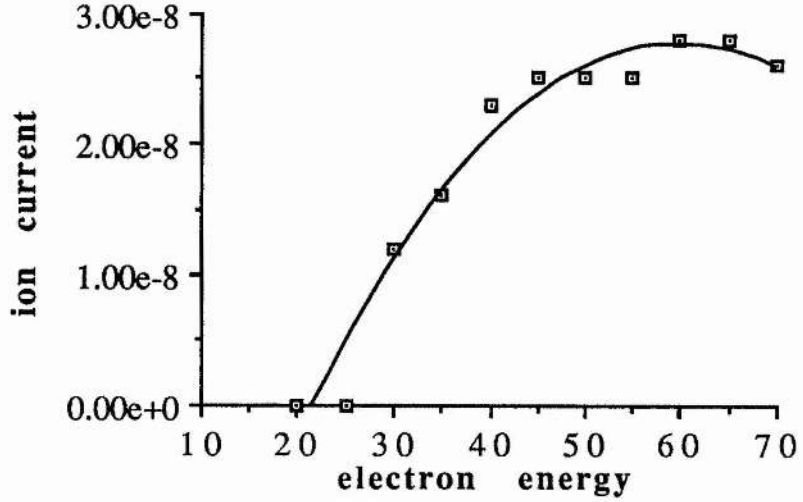
5.21. Electron energy settings versus peak height.

Table 5.2 shows how the peak height varies as the electron energy is varied. Once again the peak at m/e 28 corresponding to the N_2^+ ion of nitrogen was selected and instrumental perameters were optimized to give maximum

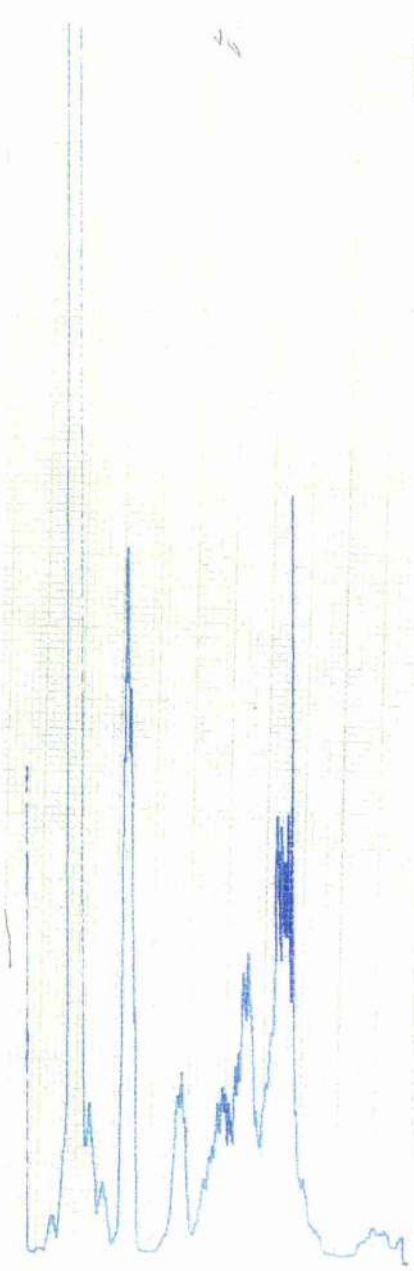
peak height for a nitrogen pressure of 1×10^{-6}mbar. The results are also shown in graph 5.2.

ELECTRON ENERGY/VOLTS	ION CURRENT/AMPS
20	0
25	0
30	1.2×10^{-8}
35	1.6×10^{-8}
40	2.3×10^{-8}
45	2.5×10^{-8}
50	2.5×10^{-8}
55	2.5×10^{-8}
60	2.8×10^{-8}
65	2.8×10^{-8}
70	2.6×10^{-8}

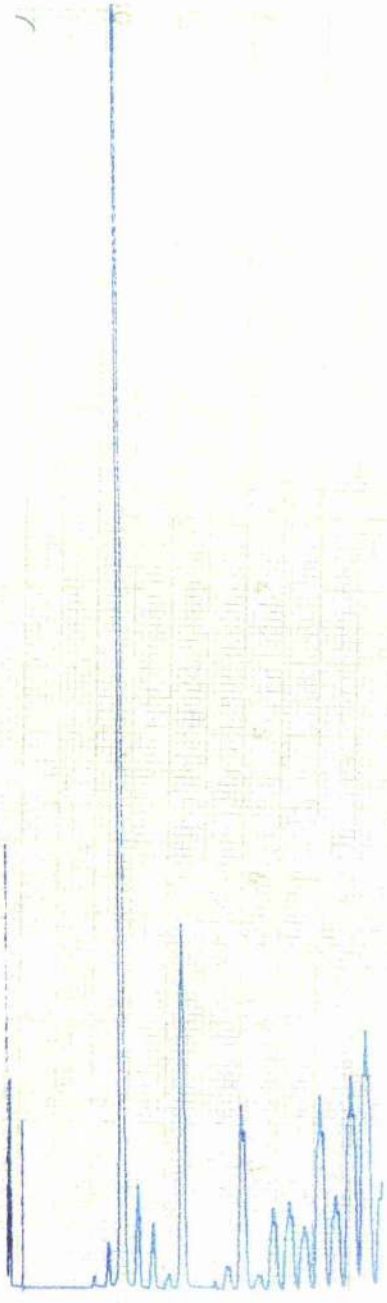
Table5.2. The relationship between electron energy and Ion current.



Graph 5.2 The variation in ion current with electron energy



Spectrum 5.1



Spectrum 5.2

The results indicate that the optimum setting for the electron energy is about 40 volts. The instrument was operated at this setting throughout this work.

5.22. Ion energy versus peak height.

Ion energy volts	Ion current Amps
5	0
10	0
15	0
20	1.4×10^{-8}
25	6.5×10^{-8}
30	2.3×10^{-7}
35	7.4×10^{-7}
40	2.5×10^{-6}

Table 5.3. The relationship between ion energy and peak height.

Table 5.3 shows the relationship between peak height and ion energy setting. As the ion energy is increased so the signal height increases. This indicates that the ion energy control is functioning correctly as an increase in ion energy corresponds to an increase in the forward velocity of the ions. However spectra5.1 and 5.2 illustrate the consequence of using a high setting of ion energy. A comparatively low ion energy setting produces a well resolved spectrum. However when the the ion energy is increased a corresponding drop in resolution can clearly be seen. This is consistent with theory as an increase in the energy imparted upon the ion serves to reduce its time spent in the

quadrupoles. The number of oscillations a particular ion makes as it passes down the quadrupole determines the resolution. The more oscillations the better the resolution. Typical ion energy operating values throughout the course of this work were between 18 and 20 eV. It should be noted that a certain ion energy must be imparted upon the ion if it is to travel the length of the instrument; settings below 15eV produced no observable signal. It was also noted that a significant increase in the ion energy resulted in differences in the ion molecule spectra observed. Once set for a particular experiment the setting was not altered. The ion energy setting for each reaction pathway investigation was kept constant throughout the experiment.

5.23. The variation in peak height and resolution with different pole bias settings.

POLE BIAS	ION CURRENT
VOLTS	AMPS
+15	4.2×10^{-9}
+12	7.0×10^{-9}
+9	2.3×10^{-8}
+6	2.4×10^{-8}
+3	2.9×10^{-8}
0	3.0×10^{-8}
- 3	3.3×10^{-8}
-6	5.2×10^{-8}
-9	5.5×10^{-8}
-12	6.1×10^{-8}
-15	7.2×10^{-8}

(n.b pole bias settings are relative to earth)

Table 5.4. The relationship between pole bias setting on the first quadrupole and peak height.

As the pole bias setting on the first quadrupole is made more positive it serves to slow the ion down. There is a decrease in the ion current as the pole bias is made more positive, however this is compensated for by an increase in the resolution of the spectrum. As the pole bias is made more negative the ions produced in the source are accelerated into the first quadrupole. There is an increase in the ion current, but a corresponding decrease in resolution. When operating the instrument the pole bias on the first quadrupole was generally set at a +9 to +12 volts positive value. It was found that throughout the course of the investigations only a fractional change in the pole bias setting on the first quadrupole altered the resolution dramatically.

5.24 Effect of altering the second quadrupole pole bias setting on a typical ion molecule reaction.

To assess the effect of altering the pole bias on the second quadrupole on an ion molecule reaction the following system was set up:

1. $CH_3OCH_3 + e^- \longrightarrow CHO^+$.....
2. $CHO^+ + C_2H_6 \longrightarrow C_2H_7^+$.....

CHO^+ was generated in the source from dimethyl ether and selected using the first quadrupole. The pressure of dimethyl ether was kept constant throughout the investigation (1×10^{-5} mbar). Ethane was passed into the

second quadrupole at a constant pressure of (8×10^{-6}mbar). The resulting ion molecule reaction was recorded at different pole bias settings of the second quadrupole. The results are shown in Table 5.5.

ION	$C_2H_4^+$	$C_2H_6^+$	$C_2H_7^+$
POLE BIAS VOLTS		% ION CURRENT	
-15	8.5	70.4	20.1
-12	8.3	68.3	23.4
-9	8.2	65.2	26.2
-6	8.9	61.3	29.6
-3	9.2	62.5	29.5
0	8.5	60.4	29.7
+3	7.3	57.2	31.5
+6	7.3	57.2	33.3
+9	6.9	57.2	34.9
+12	6.5	58.1	36.2
+15	6.5	58.3	37.9

Table 5.5. The effect of second quadrupole pole bias setting on the reaction of CHO^+ with ethane.

As can be seen from the above table the flux of the $C_2H_7^+$ ion is at a maximum when the pole bias setting on the second quadrupole is highly positive. This serves to decelerate the incoming CHO^+ ion. It has also been noted that the same effect is observed when an ion is passed from the third quadrupole into a target gas in the fourth quadrupole and recording the mass spectrum in the fifth. A positive pole bias on the second and fourth quadrupoles is required to produce a significant ion-molecule reaction.

5.3 Instrumental calibration.

The objective of this investigation was to determine the linearity of the quinquadrupole mass spectrometer mass scale. It is known that the scale on the triple quadrupole mass spectrometer becomes non-linear at masses above 150. The instrument is set up to give an upper mass limit of around m/e 200. The change in resolution at higher masses was also investigated at this stage.

A sample of n-decane was introduced into the system at a pressure of $2x10^{-6}$mbar and the spectrum was recorded. The results are shown in table5.6. It is usual to use heptacosaflurotributylamine as a mass spectromenter calibrant material. However it was felt that this might linger in the instrument for a long period of time after calibration. Also the instrument is not set up to study masses above m/e 200 there is little point introducing a calibrant material giving peaks around m/e 600

n-decane mass = 122.

Fragments.	**43**	**57**	**41**	**29**	**71**	**27**	**85**	**56**
Literature Abundance.	100	82	43	38	30	28	21	18
QQQMS.	100	75	40	38	27	26	18	21

Table 5.6. The electron impact mass spectrum of decane using the quinquaquadrupole mass spectrometer.(Literature values included for comparison).

It can be concluded from the above results that the quinquaquadrupole mass spectrometer produces essentially the same fragment ion spectra as other instruments below mass 100. The calibration of the decane spectrum indicated that there was no noticeable deviation from linearity up to mass m/e 85. It was decided not to chemically test the upper mass limit of the instrument at this stage. However during the course of this research ions have been observed up to mass m/e120. It was noticed that the resolution of high mass ions was significantly better than that of the lower masses. Perhaps a consequence of the slower velocity of the higher mass fragments, hence a longer time interval is required for them to pass through the quadrupole.

5.4.Chemical investigations

5.40 Charge exchange studies.

The performance of the instrument was investigated using a sequence of charge exchange reactions. The charge exchange system from the first to the third quadrupole and from the third to the fifth were initially studied on the triple quadrupole mass spectrometer to allow a direct comparison of the performance of the two instruments. Neon (ionization energy= 20.22eV) was ionized in the source and the Ne^+ ion was selected in the first quadrupole. Nitrogen (ionization energy=15.99 eV) was admitted into the second quadrupole as the first target gas and its pressure was progressively increased. The products were observed in the third quadrupole. The results for both the triple and

quinquadrupole mass spectrometers at various pressures are shown in tables 5.7 and 5.8.

Table5.7 Triple quadrupole mass spectrometer.

Pressure. (mbar)		m/e		
Neon.	Nitrogen.	14	20	28
		% total ion current.		
1×10^{-6}	7×10^{-6}	1.3	92.4	6.3
1×10^{-6}	1×10^{-5}	1.7	90.2	8.1
1×10^{-6}	2×10^{-5}	2.5	87.4	10.1
1×10^{-6}	8×10^{-5}	6.3	65.5	28.2
1×10^{-6}	2×10^{-4}	8.8	55.8	36.4

Table5.8 Quinquaquadrupole mass spectrometer.

Pressure. (mbar)		m/e		
Neon.	Nitrogen.	14	20	28
		% total ion current.		
1×10^{-6}	7×10^{-6}	3.0	83.7	13.3
1×10^{-6}	1×10^{-5}	5.9	70.8	23.5
1×10^{-6}	2×10^{-5}	6.6	67.9	25.5
1×10^{-6}	8×10^{-5}	9.4	54.1	36.5
1×10^{-6}	2×10^{-4}	10.5	51.3	39.2

Table5.9 Triple quadrupole mass spectrometer.

Pressure. (mbar)		m/e				
Nitrogen.	Carbon dioxide.	12	14	16	28	44
		% total ion current.				
1×10^{-6}	7×10^{-6}	0.2	90.7	0.4	2.4	6.3
1×10^{-6}	1×10^{-5}	0.2	86.3	0.5	3.3	9.7
1×10^{-6}	2×10^{-5}	0.3	83.1	0.6	3.9	12.1
1×10^{-5}	8×10^{-5}	0.5	75.4.	1.1	5.8	17.2
1×10^{-5}	2×10^{-4}	0.6	71.3	1.3	7.7	19.1

Table5.10 Quinquaquadrupole mass spectrometer.

Pressure. (mbar)		m/e				
Nitrogen.	Carbon dioxide.	12	14	16	28	44
		% total ion current.				
$1x10^{-6}$	$7x10^{-6}$	0.1	94.3	0.1	0.2	5.3
$1x10^{-6}$	$1x10^{-5}$	0.1	92.3	0.2	0.3	7.1
$1x10^{-6}$	$2x10^{-5}$	0.2	90.7	0.3	0.4	8.4
$1x10^{-5}$	$8x10^{-5}$	0.1	88.4	0.2	0.5	10.8
$1x10^{-5}$	$2x10^{-4}$	0.4	80.1	0.5	0.9	18.1

The peak at m/e 28 corresponding to the N_2^+ ion was selected from the third quadrupole and passed into carbon dioxide(ionization energy 12.11eV) in the fourth quadrupole and the product ions were observed in the fifth. The results at different target gas pressures are shown in tables 5.9 and 5.10. It was noted that inorder to observe a significant amount of product ions in the fifth quadrupole the sensitivity of the instrument had to be set to its maximum value and the fourth quadrupole pole bias setting had to be carefully adjusted. The results from both instruments are in good agreement. The peaks for the carbon dioxide fragments in the fifth quadrupole were all well defined. This was the first recorded reaction to be achieved through all five quadrupoles.

5.5 Generation and reactions of the methonium ion.

5.50 Introduction.

The generation and study of the methonium ion has proved very difficult on the triple quadrupole mass spectrometer. The peak corresponding to m/e17 is small in comparision to the other fragments and poorly resolved. A high pressure of methane is required in the ion source to produce a small CH_5^+ peak at m/e17. The peak is not only comprised of the ion current from the CH_5^+(m/e17) ion, but also contains ion current contributions from CD_2H^+, CDH_3^+, $C^{13}D_2^+$,$C^{13}DH_2^+$ and $C^{13}H_4^+$. The CH_5^+ peak is generated in the ion source by the reaction of CH_4^+ with methane;

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ \quad CH_3$$

An alternative method via which the methonium ion may be generated in a significant amount is by the reaction of methane with a suitable protonating agent in the quinquaquadrupole mass spectrometer . This is illustrated in the reaction scheme below.

Source.	Quad1	Quad 2	Quad3	Quad 4	Quad 5
Dimethyl-ether	CHO^+	CH_4	CH_5^+	TARGET GAS	PRODUCT IONS

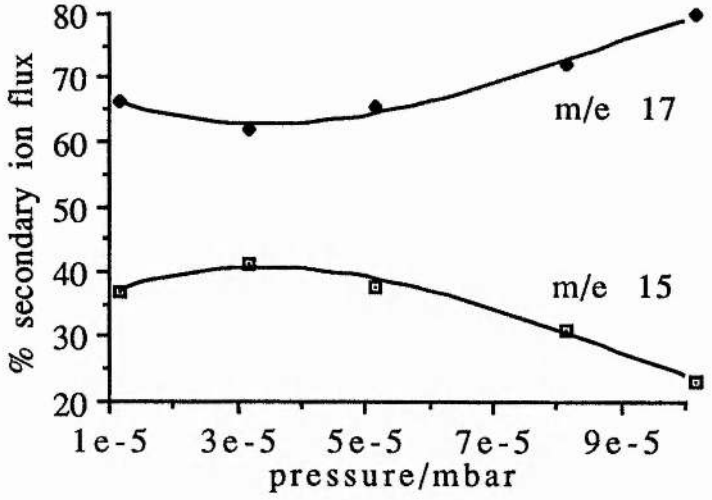
The CHO^+ ion can be generated in large abundance from a number of different sources including methanol(CH_3OH), methanoic acid (HCOOH) ethanal (CH_3CHO) and dimethyl

ether(CH_3OCH_3). Using the first three compounds as primary ion sources introduces a problem at the inlet valve. The vapours of these chemicals tend to condense in the area of the needle valve. This results in sudden surges of vapour into the source and consequently large variations in the CHO^+ ion current. Attempts have been made to counter this problem by wrapping a flexi coil heater around the inlet valve and heating it to 40 ^{0}C. This does reduce the problem, however it by no means solves it. Moreover heating the needle valve is undesirable. Dimethyl ether was selected as a suitable source of CHO^+ as its introduction has none of the previously described problems associated with it.

In the first instance the objective was to generate a sufficiently large signal of CH_5^+ in quadrupole 3 to allow it to be selected and passed into the fourth quadrupole . Table 5.11 shows the results obtained when using CHO^+ as the primary ion. The pressure of methane was progressively increased while keeping the pressure of the CHO^+ constant.

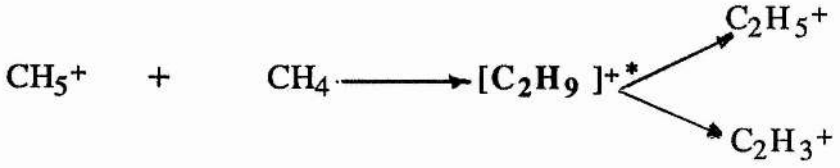
	% secondary ion current.	
Pressure of methane.(mbar)	**CH_3^+(15)**	**CH_5^+(17)**
1×10^{-5}	35.2	64.8
3×10^{-5}	39.8	60.2
5×10^{-5}	36.2	63.8
8×10^{-5}	29.4	70.6
1×10^{-4}	21.7	78.3

Table5.11. The generation of CH_5^+ at different pressures of methane.



Graph 5.3. Variation in the CH_5^+/CH_3^+ ion fluxes with varying methane pressure.

It was noted that at higher pressures of CH_4 ($>5x10^{-5}$mbar) further peaks appeared in the mass spectrum corresponding to m/e27 and 29. These corresponded to the formation of the $C_2H_5^+$ and $C_2H_3^+$ ions.



5.51 Reactions of the methonium ion.

Having successfully generated the CH_5^+ ion in the third quadrupole studies were made of its ion molecule reactions with simple alkenes. The CH_5^+ ion was selected in the third quadrupole and passed into the fourth quadrupole. Ethene was slowly passed into the fourth quadrupole. Initially only unresolved humps of peaks appeared around m/e30 and

m/e40. The pole bias and resolution controls were adjusted to give the maximum peak height for the required resolution. The adjustment of the fourth and fifth quadrupoles required a great deal of care. It was found that only fractional changes in the pole bias and resolution settings caused dramatic changes in both the height and shape of the observed peaks. The pressure of the ethene was progressively increased and a spectrum of the product ions was recorded at each increase.(table 5.12 and graph 5.4).

CH_5^+ /ethene reaction.

Results

Pressure of Ethene/mbar.	Fragment ions m/e					
	27	28	29	39	41	42
8×10^{-5}	57.2	15.2	9,3	5.7	9.2	0.4
9×10^{-5}	53.1	16.6	10.3	6.7	12.4	0.9
2×10^{-4}	46.5	18.3	11.6	6.9	15.4	1.3
4×10^{-4}	41.3	19.7	12.5	7.3	16.4	1.5

Table5.12. The CH_5^+/ethene ion molecule reaction recorded at different ethene pressures.

Graph5.4. The ethene /CH_5^+-ion molecule reaction.

The ethene/CH_5^+ system has its base peak at m/e27. This corresponds to the formation of the $C_2H_3^+$ ion.

$$CH_5^+ + C_2H_4 \longrightarrow [C_3H_9]^{+*} \longrightarrow C_2H_3^+ \ (CH_4, H_2)$$

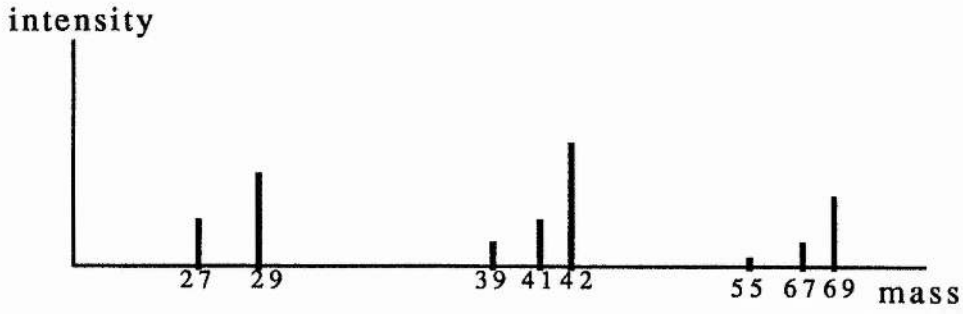
The flux of the $C_2H_3^+$ ion decreases with increasing ethene pressure indicating a further reaction, possibly the formation of $C_3H_5^+$. The flux of this ion increases with increasing ethene pressure.

The ethene was removed and propene was attached to the vacuum line. After optimising the instrumental settings the reaction of CH_5^+ with propene was recorded at different pressures of the target gas.(table 5.13 and graph 5.5).

CH_5^+/propene.

pressure of propene/mbar.	**27**	**28**	**29**	**30**	**39**	**41**	**42.**
8×10^{-5}	21.5	2.3	20.4	0.5	11.0	42.2	1.1
9×10^{-5}	21.3	2.7	16.7	1.1	9.7	46.1	2.4
2×10^{-4}	19.6	2.8	12.3	1.9	7.3	52.3	3.7
4×10^{-4}	17.4	2.9	10.5	2.1	7.5	55.7	3.9

Table 5.13. The CH_5^+/propene ion-molecule reaction recorded at different propene pressures.



Graph5.5. The propene /CH_5^+ion molecule reaction.

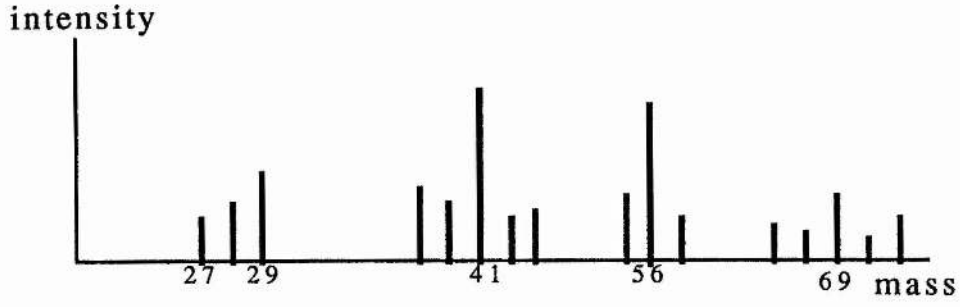
The reaction of propene with CH_5^+ has its base peak at m/e 41 corresponding to the $C_3H_5^+$ formed by an analogus route to the C_2H_4/CH_5^+ base peak. There is also a significant formation of the $C_2H_5^+$ and $C_2H_3^+$ ions. The ions of higher mass only occur at high propene pressures. They are likely to be formed as a result of tertiary reactions of the $C_2H_5^+$ ion as the flux of $C_2H_5^+$ decreases with increasing propene pressure.

$C_2H_5^+ + C_3H_6 \rightarrow [C_5H_{11}]^{+*} \rightarrow C_5H_9^+(H_2)$

$C_5H_7^+(H_2)$

pressure of	m/e									
1-butene	27	28	29	39	41	42	55	56	57	69
/mbar.										
8×10^{-5}	4.8	7.5	8.5	7.9	15.1	4.8	8.9	14.0	4.9	4.8
9×10^{-5}	5.3	7.6	8.9	9.2	18.5	4.7	9.3	16.4	4.8	5.3
2×10^{-4}	5.8	7.2	8.5	9.9	20.7	3.9	11.4	18.3	4.3	6.2
4×10^{-4}	5.5	6.9	8.3	9.7	21.7	3.3	13.2	17.5	3.7	6.5

Table5.14 The 1-butene/CH_5^+ ion molecule reaction.



Graph5.6. The 1-butene /CH_5^+ion molecule reaction.

As indicated by graph 5.6 there are a number of minor ions which resulted from tertiary processes at higher pressures. The major ions formed were the $C_4H_8^+$ ion by charge exchange with the CH_5^+ and the $C_3H_5^+$ ion. As the pressure of 1-butene was increased it became difficult to resolve all the peaks in the spectrum. The instrument had to be set to highest attenuation before all of the ions became visible. The pressure was not increased any further as this would have damaged the multiplier which was already functioning at its limit(this was indicated by ripples in the base line of the spectra.)

5.6 Generation and reaction of the ethonium ion ($C_2H_7^+$).

5.60 Introduction.

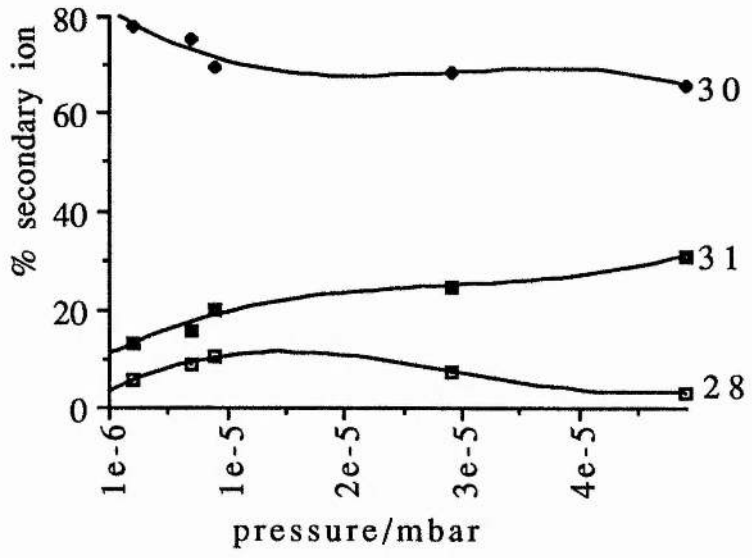
As an extension to the study of the ion molecule reactions of protonated alkanes an attempt was made to generate the ethonium($C_2H_7^+$). The instrument was set up in the following way:

Source.	Quad 1.	Quad 2.	Quad 3.	Quad 4.	Quad 5.
Dimethyl-ether	CHO^+	C_2H_6	$C_2H_7^+$	Target gas	Product ions.

Dimethyl ether was passed into the ion source at an initial pressure of $4x10^{-6}$mbar. Instrumental parameters were optimized to give the best peak heights for the required resolution and the CHO^+ ion was selected and passed into the second quadrupole. Ethane was passed into the second quadrupole at an initial pressure of $3x10^{-6}$mbar. The pole bias setting on the second quadrupole was altered to give the optimum peak height of $C_2H_7^+$ and the spectrum was recorded in the third quadrupole. The pressure of ethane was progressively altered, keeping all other parameters constant and the principal product ions were recorded each time. The results are shown in table5.15 and graph 5.7.

Pressure mbar.	$3x10^{-6}$	$8x10^{-6}$	$1x10^{-5}$	$3x10^{-5}$	$5x10^{-5}$
Ion					
$C_2H_4^+$	5.5	9.0	10.4	7.5	3..3
$C_2H_6^+$	78.1	75.2	69.4	68.4	68.5
$C_2H_7^+$	13.3	15.8	20.1	24.0	30.9

Table 5.15 The effect of target ion pressure on the generation of the $C_2H_7^+$ ion.



Graph5.7. The reaction of CHO^+ with ethane at different ethane pressures.

There are a number of minor ions produced as the pressure of ethane is increased. The most significant of these minor ions is the $C_2H_5^+$ ion. At mass m/e29 is is not possible to measure the % of this ion produced as the CHO^+(m/e29) peak lies on top of it. However its formation was confirmed by repeating the generation of $C_2H_7^+$ using CH_2N^+(m/e28) as the proton transfer ion.

$CH_3NH_2 + e^-$ → CH_2N^+**(m/e28)**

C_2H_6

$C_2H_5^+$ $C_2H_6^+$

$C_2H_7^+$

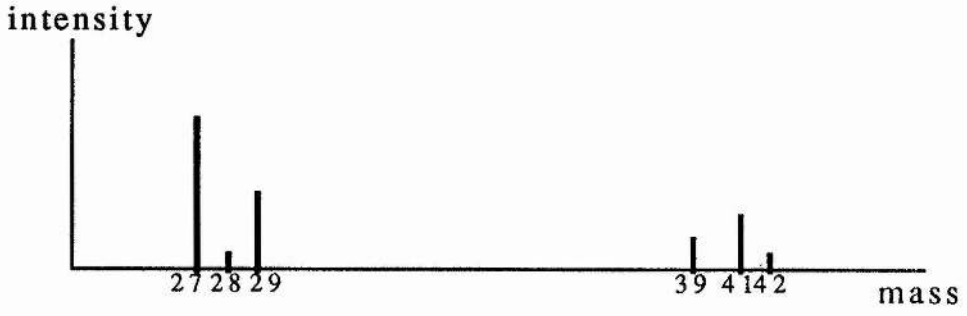
Figure5.1 Generation of the ethonium ion using CH_2N^+

The other minor ions produced are the CH_3^+, $C_2H_5^+$, $C_2H_3^+$, $C_3H_5^+$, $C_4H_7^+$ and $C_4H_9^+$ ions.

As with the investigations involving the methonium ion the ethonium ion was selected and reacted in turn with simple alkenes; in this case propene and 1-butene.

Pressure of 1-butene/mbar	27	28	29	39	41	42
8 x10^{-5}	44.3	2.6	20.9	11.2	19.0	1.9
9 x10^{-5}	40.7	2.9	22.6	12.1	21.0	1.8
2 x10-4	34.3	2.8	24.7	13.3	22.1	1.5
4x10-4	30.2	2.9	28.2	15.8	27.9	1.3

Table5.16. The $C_2H_7^+$/propene ion-molecule reaction recorded at different propene pressures.



Graph5.8. The propene /$C_2H_7^+$ion molecule reaction.

The principal product ion from the reaction of propene with $C_2H_7^+$ is the $C_2H_3^+$ ion (ref graph 5.8). The flux of this ion decreases with increasing propene pressure. As there are no tertiary product ions present as the propene pressure is increased it is likely that the precursor ion to the $C_2H_3^+$ fragment is being collisionally stabilised.

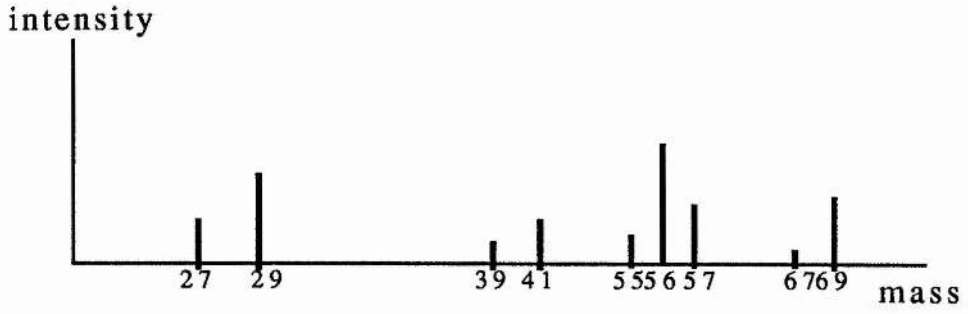
The likely precursor to the $C_2H_3^+$ ion is the $C_2H_5^+$ ion. The relative flux of this ion increases with increased propene pressure. It is interesting to note that there is no evidence of the presence of proton transfer to propene from the $C_2H_7^+$ion.

In the corresponding $C_2H_7^+$/1-butene reaction the product of proton transfer is observed (ref table 5.17 and graph 5.9).

	m/e							
Pressure of 1-butene/mbar	**27**	**29**	**39**	**41**	**55**	**56**	**57**	**69**
	% secondary ion current.							
8 x10^{-5}	10.2	15.9	5.8	12.6	3.8	22.7	13.1	12.7
9 x10^{-5}	9.6	13.8	5.6	13.1	2.9	18.4	16.1	16.2
2 x10^{-4}	7.3	11.3	4.2	16.1	2.7	14.3	21.1	19.5
4 x10^{-4}	7.0	10.8	4.3	18.8	2.9	12.4	25.2	22.6

Table 5.17. The $C_2H_7^+$/1-butene ion-molecule reaction recorded at different propene pressures.

(n.b Major ion fluxes included.)



Graph5.9. The 1-butene /$C_2H_7^+$ion molecule reaction.

At lower pressures the1-butene/$C_2H_7^+$ ion molecule reaction shows a base peak at m/e56 corresponding to the charge exchange product ion. Significant fluxes of the $C_2H_5^+$, $C_3H_5^+$, $C_4H_9^+$ and $C_5H_9^+$ ions are also present throughout the pressure range studied. The flux of the tertiary $C_5H_9^+$ ion increases with increased 1-butene pressure. It is likely to be formed from the reaction of the $C_2H_5^+$ ion with 1-butene.

$$C_2H_5^+ + C_4H_8 \longrightarrow [C_6H_{13}]^{+*} \longrightarrow C_5H_9^+(CH_4) \quad C_5H_7^+(H_2)$$

n.b

As the pressure of 1-butene is increased the ion at m/e 57 corresponding to the $C_4H_7^+$ ion becomes the dominant product.

5.7 Conclusions to the CH_5^+ and $C_2H_7^+$ investigations.

The generation of both the CH_5^+ and $C_2H_7^+$ ions has been accomplished using the first three quadrupoles of the quinquaquadrupole mass spectrometer. The reactions of these ions with simple linear alkenes have also been

achieved in the fourth and the fifth quadrupoles. The major problem of insufficent transmission of the $CH_5^+/C_2H_7^+$ ions from the third to the fourth quadrupole has now been overcome. There is great potential to extend the use of the quinquaquadrupole mass spectrometer to study the reactions of transient ions with a huge number of target molecules. Ions such as $CCl_xH_yF_z$ (where x+y+z=5) could be generated and their reactions studied. The generation of the OH^+ from a number of precursors ion was attempted without success during the course of this research. The difficulty is generating it in sufficient quantities to be transfered from the third to the fourth quadrupole. This merits further investigation.

5.8 Reaction sequence elucidation studies.

3.80 Introduction.

As described in chapter 4 a major difficulty when studying ion molecule reactions using triple quadrupole mass spectrometry is the unambiguous elucidation of reaction pathways. The use of modelling systems is often employed when using the triple quadrupole mass spectrometer, however this technique has limitations in that it is extremely time consuming and can sometimes lead to spurious results. The quinquaquadrupole mass spectrometer provides a method for the rapid and unambiguous determination of reaction pathways.

5.81 The ethenyl ion molecule reaction.

The reaction of the ethenyl radical cation with ethene has been studied by a number of different research groups using a number of different techniques[105,106]. The study of this reaction on the quinquaquadruopole mass spectrometer was undertaken to assess the reproducibility of the instrument and also in an attempt to obtain a more detailed understanding of the secondary and tertiary ion molecule reactions occuring.

Initially the instrument was set up as a triple quadrupole mass spectrometer, the ethenyl radical cation was selected in the first quadrupole and passed into ethene in the second quadrupole. The product ions were mass analysed in the third quadrupole with quadrupoles four and five operated in the total ion mode. Figure 5.2 shows the ions produced in this reaction.

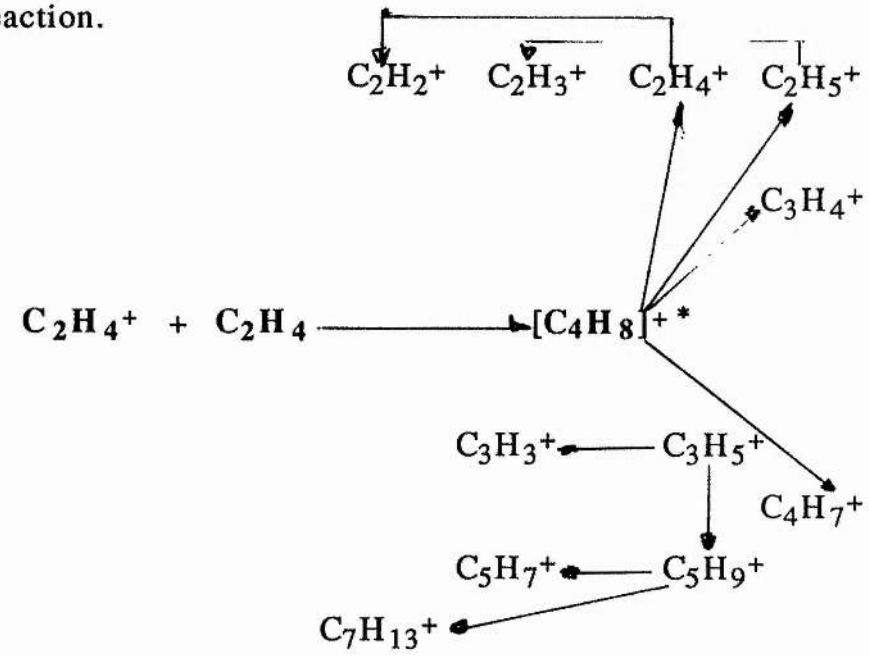


Figure5.2 The ethenyl radical cation /ethene ion- molecule reaction.

The pressure of the ethene target gas was varied and the variation of product ion currents was recorded. The results are shown in table 5.18

	m/e							
Pressure of ethene/mbar	**29**	**39**	**41**	**53**	**55**	**67**	**69**	**83**
Low pressure ($5x10^{-6}$mbar)	2.9	2.1	35.6	1.2	2.7	1.9	4.7	-
High pressure ($2x10^{-4}$mbar)	2.3	6.4	13.8	4.2	6.7	8.3	27.8	9.7

n.b major ions included in the table.

Table5.18 The ethenyl ion molecule reaction.

The major product ion is the $C_3H_5^+$ which is formed as shown below.

$$C_2H_4^{+\bullet} + C_2H_4 \longrightarrow [C_4H_8]^{+*} \longrightarrow C_3H_5^+ (CH_3^\bullet)$$

The quinquaquadrupole mass spectrometer was set up in the following way

$C_2H_4 + e^-$ _____ $C_2H_4^+, C_2H_3^+, C_2H_2^+$ etc	**SOURCE**
	QUAD .1.
C_2H_4	**QUAD .2.**
$C_2H_2^+, C_2H_3^+, C_2H_5^+, C_3H_4^+, C_3H_3^+,$	**QUAD .3.**
$C_3H_5^+, C_4H_7^+, C_5H_7^+, C_5H_9^+, C_6H_{11}^+$ etc	
C_2H_4	**QUAD .4.**
Product ions from each reaction.	**QUAD .5.**

Ethene was admitted into the fourth quadrupole and the different product ions were selected from the third quadrupole. The individual ion molecule reactions were

analysed using the fifth quadrupole. Using the quinquadrupole mass spectrometer in this way provides a direct method for the determination of the tertiary and higher order ion reaction pathways. Each of the reactions will be discussed in turn.

Selection of $C_3H_5^+$ ion.

The $C_3H_5^+$ ion reacts with ethene in the fourth quadrupole to produce the following ions;

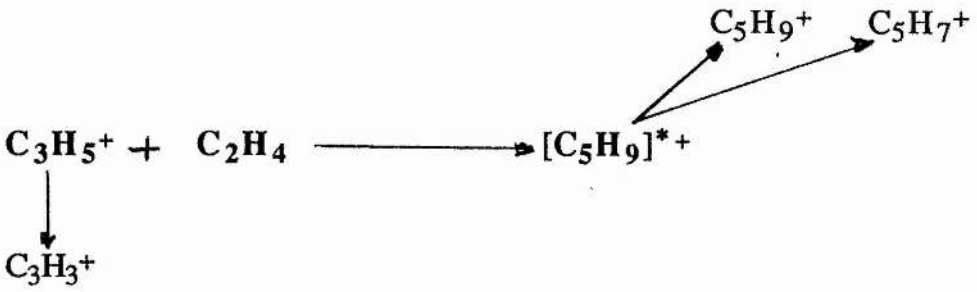


Figure 5.3 Reaction of the $C_3H_5^+$ ion with ethene.

As the pressure of the ethene is increased the flux of all the product ions increases. The $C_5H_9^+$ ion is the dominant tertiary fragment throughout the entire pressure range.

Selection of the $C_5H_9^+$ ion.

By resetting the third quadrupole to allow only the $C_5H_9^+$ ion into the and passing nitrogen into the fourth the product ions from the collision induced dissociation of the ion could be observed. Ions of mass 67, 41, 39, 29, 27 were observed.

The fragmentation is depicted below,

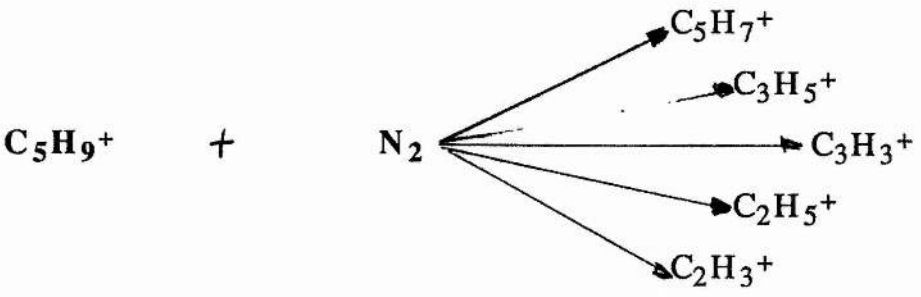


Figure 5.4 Fragmentation of the $C_5H_9^+$ ion.

The presence of the above ions in the CID fragmentation spectrum of indicates that the dissociation of the $C_5H_9^+$ ion contributes in part to the flux of these fragments.

Selection of the $C_5H_7^+$ ion.

Reselection of the $C_5H_7^+$ ion was carried out. This ion was then passed into nitrogen at the same pressure as in the $C_5H_9^+$ ion case.

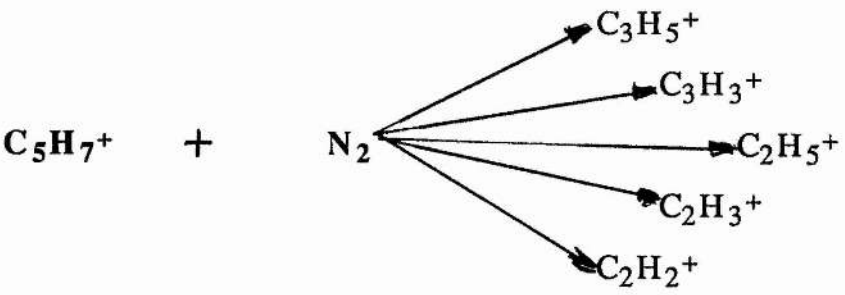


Figure 5.5 fragmentationof the $C_5H_7^+$ ion.

Selection of the $C_3H_3^+$

Confirmation that the $C_3H_3^+$ ion is derived from the loss of Hydrogen from the $C_3H_5^+$ was achieved by passing $C_3H_5^+$ into nitrogen.

$$C_3H_5^+ + N_2 \longrightarrow C_3H_3^+ + H_2$$

When the $C_3H_3^+$ is selected and passed into ethene the major ion produced is again the $C_3H_5^+$ ion.

$$C_3H_3^+ + C_2H_4 \longrightarrow [C_5H_7]^{+*} \longrightarrow C_3H_5^+$$

As the pressure of ethene is increased a peak corresponding to the formation of the $C_5H_9^+$ ion becomes visible. This is likely to be the result of the reaction of $C_3H_5^+$with ethene, and is further confirmation of the origin of the $C_5H_9^+$ ion It can also be noted that an increase in ethene pressure results in an increase in the $C_5H_7^+$ ion. This can be attributed to the increase in collisional stabilization of the $C_5H_7^+$ ion.

Selection of the $C_4H_7^+$ ion.

The $C_4H_7^+$ ion is not present in any of the reaction schemes of ions selected in from the third quadrupole and reacted with ethene in the fifth. It does however appear in the overall reaction scheme. It must therefore be concluded that it is formed as as direct result of the $C_2H_4^+/C_2H_4$ reaction.

$C_2H_4^+ + C_2H_4 \quad [C_4H_8]^{+*} \longrightarrow C_4H_7^+(H)$

Selection of the $C_4H_7^+$ ion from the third quadrupole and further reaction of the ion with ethene in the fifth quadrupole yielded $C_2H_3^+$, $C_2H_5^+$, $C_4H_5^+$ and at high ethene pressures the $C_6H_{11}^+$ ion.

$$C_4H_7^+ + C_2H_4 \longrightarrow C_6H_{11}^+$$

It must be stressed that at different reactant pressures the relative contribution results will vary significantly. Ions may react further or be collisionally stabilized by non reactive collisions.

A study of the variation in ion fragmentation/stability over a wide pressure range would be interesting to undertake. However time constraints prevents an even more in depth study of the system. The reproducibility of each system was checked to allow for any pressure fluctuations and instrumental anomalies. The results were obtained in duplicate and in most cases were in good agreement with one another.

5.82 Conclusions.

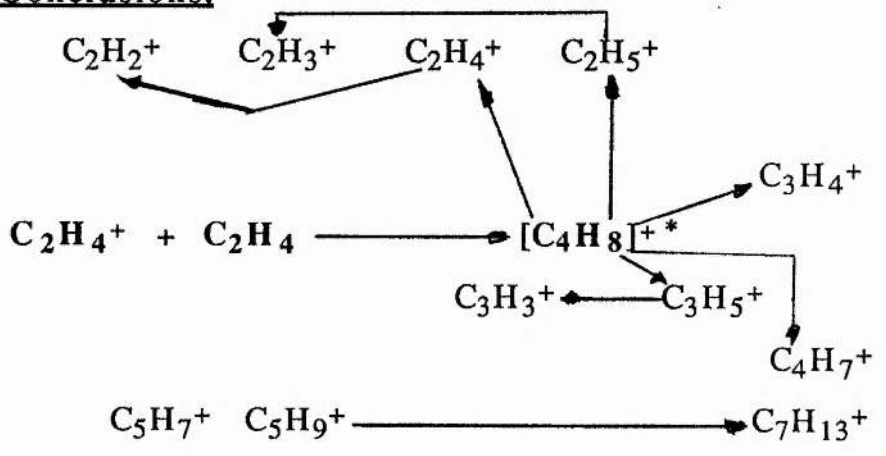


Figure 5.6 The ethenyl/ethene ion molecule reaction studied using the quinquaquadrupole mass spectrometer.

Figure 5.7 represents the ethenyl radical cation/ethene ion molecule reaction scheme studied using the quinquaquadrupole mass spectrometer. The study has given a greater insight into this system than was previously possible using the triple quadrupole mass spectrometer. Further instrumental improvements would lead to more rapid data acquisition and undoubtedly an even greater advancement in the understanding of systems such as this. It was decided to investigate both the propenyl ion molecule reaction using the same set up of the quinquadquadrupole mass spectrometer . These systems had previously been studied using a number of different techniques[107]. The propenyl radical cation/propene ion molecule reaction presents an even more complex problem due to the increase in the number of ions present.

5.83 The propenyl ion-molecule reaction.

Introduction.

It was decided to examine this system for two reasons. Firstly there is some disagreement as to the reaction pathways to the higher molecular weight ions, it was hoped that the quinquaquadrupole mass spectrometer could be used to ascertain all the major reaction routes. Secondly it it an extremely complicated system and therefore ideal to assess the performance of the instrument.

Propene was fragmented in the ion source and the $C_3H_6^+$ ion was selected in the first quadrupole(pressure $5x10^{-6}$mbar).

Propene gas was passed into the second quadrupole and the product ions were mass analysed in the third quadrupole. All ions observed from m/e26 to m/e111 in previous investigations of this system were observed in the third quadrupole. Table 5.19 illustrates the effect of varying the target gas pressure. The results obtained were compared with results obtained from the triple quadrupole mass spectrometer at comparable target gas pressures

LP=1x10^{-6}mbar. **HP**= 1X10-4mbar.

M/E	ION	%ION CURRENT T.Q.M.S		%ION CURRENT Q.Q.Q.M.S	
		LP	HP	LP	HP
26	$C_2H_2^+$	-	0.5	0.3	0.4
27	$C_2H_3^+$	-	1.2	0.9	1.9
29	$C_2H_5^+$	-	1.2	0.7	1.7
39	$C_3H_3^+$	0.5	2.7	1.1	3.3
40	$C_3H_4^+$	0.1	0.2	0.1	0.1
41	$C_3H_5^+$	3.4	9.3	2.7	10.5
43	$C_3H_7^+$	3.1	13.2	6.4	13.5
54	$C_4H_6^+$	1.7	3.7	0.2	0.9
55	$C_4H_7^+$	2.1	1.0	1.3	1.7
56	$C_4H_8^+$	9.3	10.2	1.4	14.3
57	$C_4H_9^+$	3.5	14.9	2.4	15.3
67	$C_5H_7^+$	-	2.3	0.2	1.8
68	$C_5H_8^+$	-	1.1	-	0.3
69	$C_5H_9^+$	8.4	9.3	0.5	7.0
70	$C_5H_{10}^+$	2.7	6.4	0.1	5.2
71	$C_5H_{11}^+$	T	4.3	0.2	3.9
81	$C_6H_9^+$	-	1.8	0.3	2.4
83	$C_6H_{11}^+$	T	2.1	0.4	3.7
84	$C_6H_{12}^+$	-	0.1	0.1	2.2
85	$C_6H_{13}^+$	-	3.6	0.1	1.5
97	$C_7H_{13}^+$	T	2.4	0.3	0.7
98	$C_7H_{14}^+$	T	0.1	0.1	2.3
99	$C_7H_{15}^+$	0.1	1.3	0.1	1.7

Table 5.19. The propenyl ion molecule reaction

N.B The letter T indicates a trace of the ion was observed.

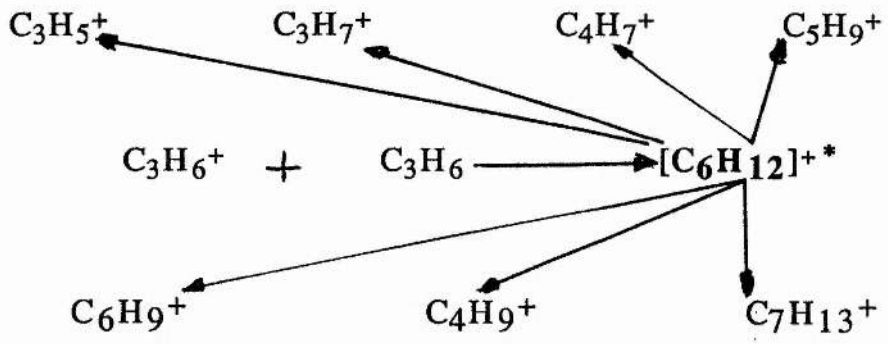


Figure5.8 The $C_3H_6^{\pm}/C_3H_6$ molecule reaction.

It can be seen that the results are in quite close agreement. By setting the quinquaquadrupole up as prevously described for the ethenyl cation/ethene ion molecule reaction it was possible to determine the source of each tertiary and higher order ions. Each ion was systematically selected and reacted with a further molecule of propene in quadrupole four. The results were analysed in the fifth quadrupole. The major ions were also selected from the third quadrupole and passed into nitrogen in the fourth quadrupole to determine the fragmentation pattern of each. The pressure of nitrogen in the fourth was always set at $1X10^{5}$mbar. The results will be discussed in turn.

The major ions produced are the $C_3H_7^+$, $C_4H_7^+$, $C_4H_8^+$ and $C_5H_9^+$ ions. As the pressure of propene is increased the ion at mass 57 becomes significant. At pressures of target gas above $5x10^{-5}$mbar it becomes the dominant ion in the spectrum.

Selection of the $C_4H_9^+$ ion.

Selection of the $C_4H_9^+$ ion from the third quadrupole and passing it into nitrogen in the fourth produced the following fragmentation pattern.

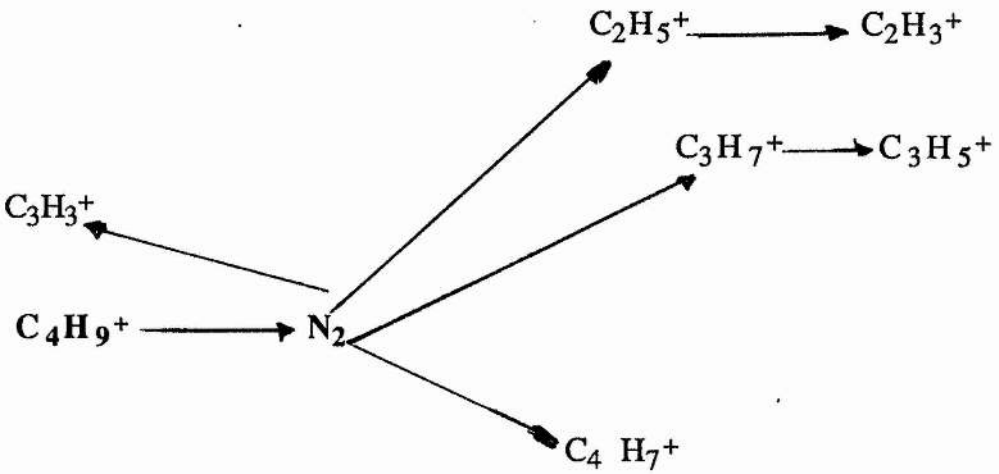


Figure 5.9 Fragmentation of the $C_4H_9^+$ ion.

The major product is the $C_3H_5^+$ ion. From previous studies (ethenyl ion molecule reaction) it can be assumed that the major flux of the $C_3H_5^+$ ion is derived from the $C_3H_7^+$ ion. When selected and passed into propene the principle ions formed was the $C_5H_9^+$ ion with also a minor flux of $C_7H_{13}^+$.

Selection of the $C_3H_7^+$ ion.

Selection of the $C_3H_7^+$ ion from the third quadrupole and passing it into propene in the fourth quadrupole produced the following reaction scheme.

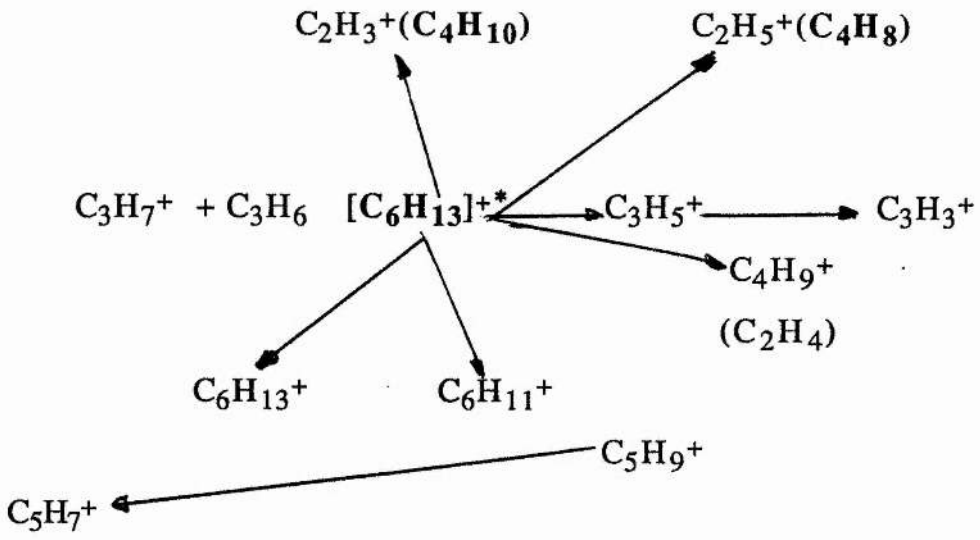


Figure 5.10 The $C_3H_7^+/C_3H_6$ ion molecule reaction.

The major ion in the $C_3H_7^+/C_3H_6$ ion molecule reaction is the $C_4H_9^+$ ion.

$$C_3H_7^+ + C_3H_6 \longrightarrow [C_6H_{13}]^{+*} \longrightarrow C_4H_9^+ + C_2H_4$$

As the pressure of propene was increased the flux of $C_4H_9^+$ increases. The $C_4H_9^+$ ion is also the dominant ion in the $C_4H_7^+$ and $C_4H_8^+$/propene ion molecule reactions.

$$C_4H_7^+ + C_3H_6 \longrightarrow [C_7H_{13}]^{+*} \longrightarrow C_4H_9^+ + C_3H$$

$$C_4H_8^+ + C_3H_6 \longrightarrow [C_7H_{14}]^{+*} \longrightarrow C_4H_9^+ + C_3H_5$$

The $C_4H_7^+$/propene and $C_4H_8^+$/propene reactions were carried out at the same pressure as the $C_3H_7^+$/propene reaction. From this set of reactions it can be concluded that the $C_3H_7^+$/propene is the dominant reaction pathway to the

$C_4H_9^+$ ion. The $C_4H_7^+$/propene and $C_4H_8^+$/propene ion molecule reactions combined produce between 15% and 24% of the $C_4H_9^+$ ion flux at low propene pressures(<3X10^{-6} mbar) and 24% to 33% of the flux at high propene pressures(3x10^{-6} - 4x10^{-4} mbar).

Selection of $C_4H_7^+$ ion.

As previously stated the $C_4H_7^+$/propene reaction is responsible for the formation of the $C_4H_9^+$ ion. Also present in the $C_4H_7^+$/propene system were;

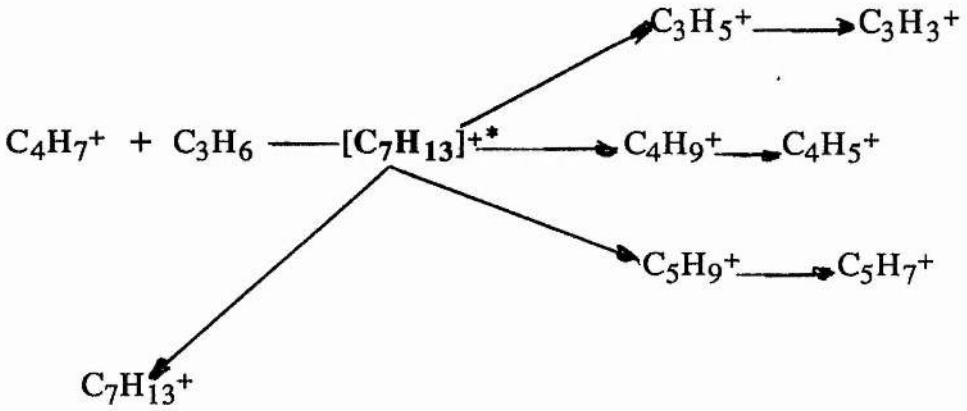
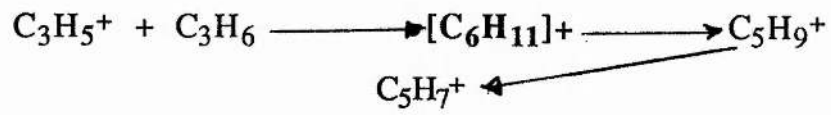


Figure5.11 The reaction of the $C_4H_7^+$ ion with propene

The major contributor to the flux of the of the $C_5H_9^+$ ion is the reaction of $C_3H_5^+$ with propene



However this is not the major route to the $C_5H_9^+$ ion. The major flux of this ion is produced by the direct reaction of the propenyl radical cation with propene.

$$C_3H_5^+ + C_3H_6 \longrightarrow [C_6H_{12}]^{+*} \longrightarrow C_5H_9^+ \ (CH_3\cdot)$$

Selection of $C_5H_9^+$

The $C_5H_9^+$ ion when passed into nitrogen produced the following fragmentation pattern.

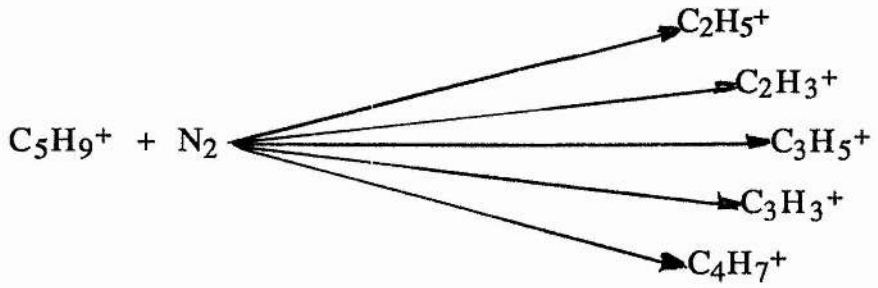


Figure5.12 fragmentation of the of the $C_5H_9^+$ ion.

Again the $C_4H_7^+$ ion is derived from more than one route. The principle contribution to the $C_4H_7^+$ ion flux is the direct reaction of $C_3H_6^+$ with propene.

$$C_3H_6^+ + C_3H_6 \longrightarrow [C_6H_{12}]^{+*} \longrightarrow C_4H_7^+ + C_2H_5$$

The $C_4H_7^+$ ion is also formed from the fragmentation of the $C_4H_9^+$ ion.

Selection of the $C_4H_8^+$ ion.

The $C_4H_8^+$ ion was selected in the third quadrupole and passed into nitrogen in the fourth. The following was observed:-

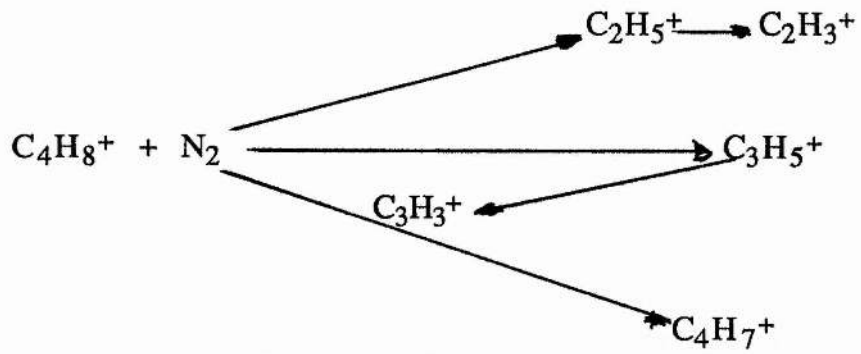


Figure5.13 Fragmentation of the $C_4H_8^+$ ion

The major fragment is the $C_3H_5^+$ ion which contributes 40% of the secondary ion flux. The $C_4H_8^+$/propene ion molecule reaction was then studied by passing $C_4H_8^+$ directly into propene. The principal product from this reaction was the $C_5H_{10}^+$ ion at m/e 70. Also present in significant quantities were the $C_4H_9^+$ ion.. As the pressure of propene was increased to $1x10^{-4}$ mbar the ions at m/e 84($C_6H_{12}^+$) and 98($C_7H_{14}^+$) became visible.

5.84 Conclusions.

The quinquaquadupole mass spectrometer has been shown by the ethenyl ion/ethene and propenyl ion/propene reactions to be capable of generating a great deal of information concerning fragmentation patterns. To study more complicated systems than the ones described it would be desirable to link the instrument to a data base. This would considerably reduce the time required for data interpretation.

The generation of a completely resolved spectrum over a mass range of m/e 20 to 100 in the fifth quadrupole from a series of reactions has now also been achieved.

5.85 Structure elucidation studies.

Introduction.

In the preceding section nitrogen was used as a neutral target in the fourth quadrupole to cause collisional dissociation of different fragment ions from the ion molecule reaction under investigation. The possibility of more extensive collisional dissociation of fragments has previously been discussed in chapter four. Inorder to use the quinquqaquadrupole mass spectrometer in this way it would be necessary to build up a data bank of the fragmentation patterns of individual ionic fragments. This could then be used to identify unknown compounds and distinguish between compounds having similar electron impact mass spectra. However the usefulness of the instrument in structural problem solving was examined using the following investigation.

Two compounds were selected which had similar electron impact mass spectra. These were cyclohexane and trans-3-hexene.

Initially a number of different fragment ions of known composition would be collisionally dissociated using the quinquaquadrupole mass spectrometer in the following way.

Source	Quad1	Quad2.	Quad3.	Quad4.	Quad5.
Gas X	X^+	N_2	Fragment spectrum.	Total ion.	Total ion.

For this example only a limited number of fragmentation patterns would be required. The two compounds were ionised by electron impact and the molecular ion from each was collisionally fragmented by selection of the appropriate ion from the first quadrupole and passing it into nitrogen at a pressure of $5x10^{-5}$ mbar in the second quadrupole. The resulting spectrum was recorded in the third quadrupole. Major fragment ions from the collisional dissociation of each sample were then selected in the third quadrupole and collisionally dissociated in the fourth by passing into nitrogen. The resulting spectra were recorded in the fifth quadrupole. By selection of the major ions produced from each sample in the third quadrupole and secondary ion fragmentation in the fourth quadrupole it is possible to very rapidly build up a detailed primary and secondary fragmentation scheme for each sample. It is extremely important to keep all instrumental parameters constant throughout each investigation and from sample to sample. The individual pressures of primary ion source gas, second quadrupole collision gas and fourth quadrupole collision gas were all kept constant throughout the investigations. Once optimized the instrumental controls were not altered.

The electron impact mass spectra of each compound was recorded by operating the instrument with the first quadrupole acting as the mass filter and the other quadrupoles operating in the total ion mode. The results were compared with the literature values[98] and found to be in good agreement. The ions and relative abundances are shown in table 5.20.

Ion m/e	56	84	41	55	42	69	39	27
Literature.								
Cyclohexane	100	77	58	33	28	24	21	19
Tr-3-Hexene	28	36	81	100	70	30	39	40
QQQMS.								
Cyclohexane	100	66	63	37	25	19	21	25
Tr-3-Hexene	33	36	79	100	67	27	38	35

Table5.20 Electron impact mass spectra of Cyclohexane and *trans*-3-hexene

The molecular ion from cyclohexane (84) was selected and passed into nitrogen in the second quadrupole the spectra of the resulting fragments was recorded in the third quadrupole. The same procedure was adopted for trans-3-hexene. The results are shown in table 5.21.

Ion m/e	56	69	41	55	39	42	27
Cyclohexane	100	55	37	38	19	12	7
Tr-3-hexene	13	18	42	100	22	10	2

Table 5.21 The CID fragmentetion of cyclohexane and *tr* 3 hexene

It can be seen that again there is a difference between the spectra of the two compounds The $C_4H_8^+$ is the base peak in the cyclohexane CID spectrum. In the Trans-3- hexene CID spectrum the base peak corresponds to the $C_4H_7^+$ ion.

The major fragment ions from the collisional fragmentation of cyclohexene were then systematically selected from the third quadrupole and passed into nitrogen in the fourth quadrupole. The spectra of the resulting fragments was recorded in the fifth quadrupole. The process was repeated under the same conditions of pressure and instrumental parameters for the *trans*-3-hexene. The results are shown in tables 5.22 and 5.23

Fragments	27	29	39	40	41	43	55	57
Ion								
$C_4H_7^+$	5	12	3	*	15	25	*	*
$C_4H_8^+$	*	*	2		19	17		
$C_5H_9^+$	5	7	15		49	*	9	

Table 5.22 The secondary ion fragments of cyclohexane.

Fragments	27	29	39	40	41	43	55	57
	$C_2H_3^+$		$C_3H_3^+$		$C_3H_5^+$		$C_4H_7^+$	
		$C_2H_5^+$		$C_3H_4^+$		$C_3H_7^+$		$C_4H_9^+$
Ion								
$C_4H_7^+$	5	13	2	*	15	7		*
$C_4H_8^+$	3	9	4	*	19			
$C_5H_9^+$		5	7	15	37	*	9	15

Table5.23 The secondary ion fragmentation of *trans*-3-hexene.

Comparison of the secondary fragmentation patterns shows that there is a difference in the relative abundance of secondary fragments produced from each of the major ions. The $C_3H_5^+$ ion is the most abundant in the six secondary schemes and its flux varies from ion to ion and to a certain extent from compound to compound. There is again a need for a data base to be connected to the quinquaquadrupole mass spectrometer if it is to be used for the identification of complicated unknowns. A set of standard conditions would also have to be arrived at. However the above scheme illustrates the way in which such a procedure could be used.

5.9 Conclusions

The chemical investigations carried out so far on the quinquaquadrupole mass spectrometer have served to illustrate the potential of the instrument. Although some of the systems examined have been relatively simple the instrument has been shown to be useful for both reaction pathway elucidation and the study of ion molecule reactions of transient ions such as CH_5^+. Although there are still a number of instrumental problems which require further investigation the instrument is essentially operating satisfactorily. If a revision of the pumping system is undertaken the range over which these reactions could be carried out would be increased. The identification of specific molecules using the instrument might also be investigated further.

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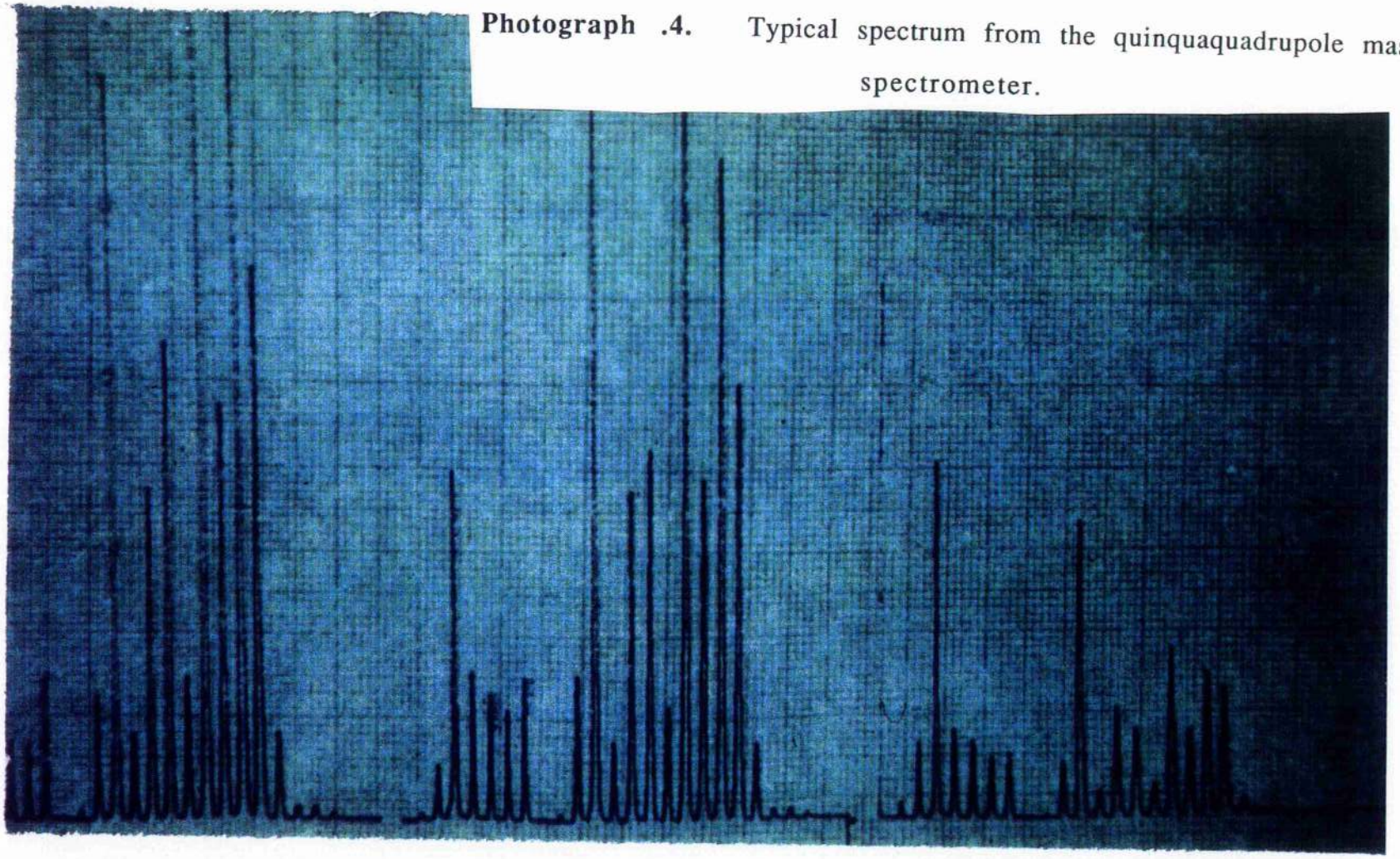
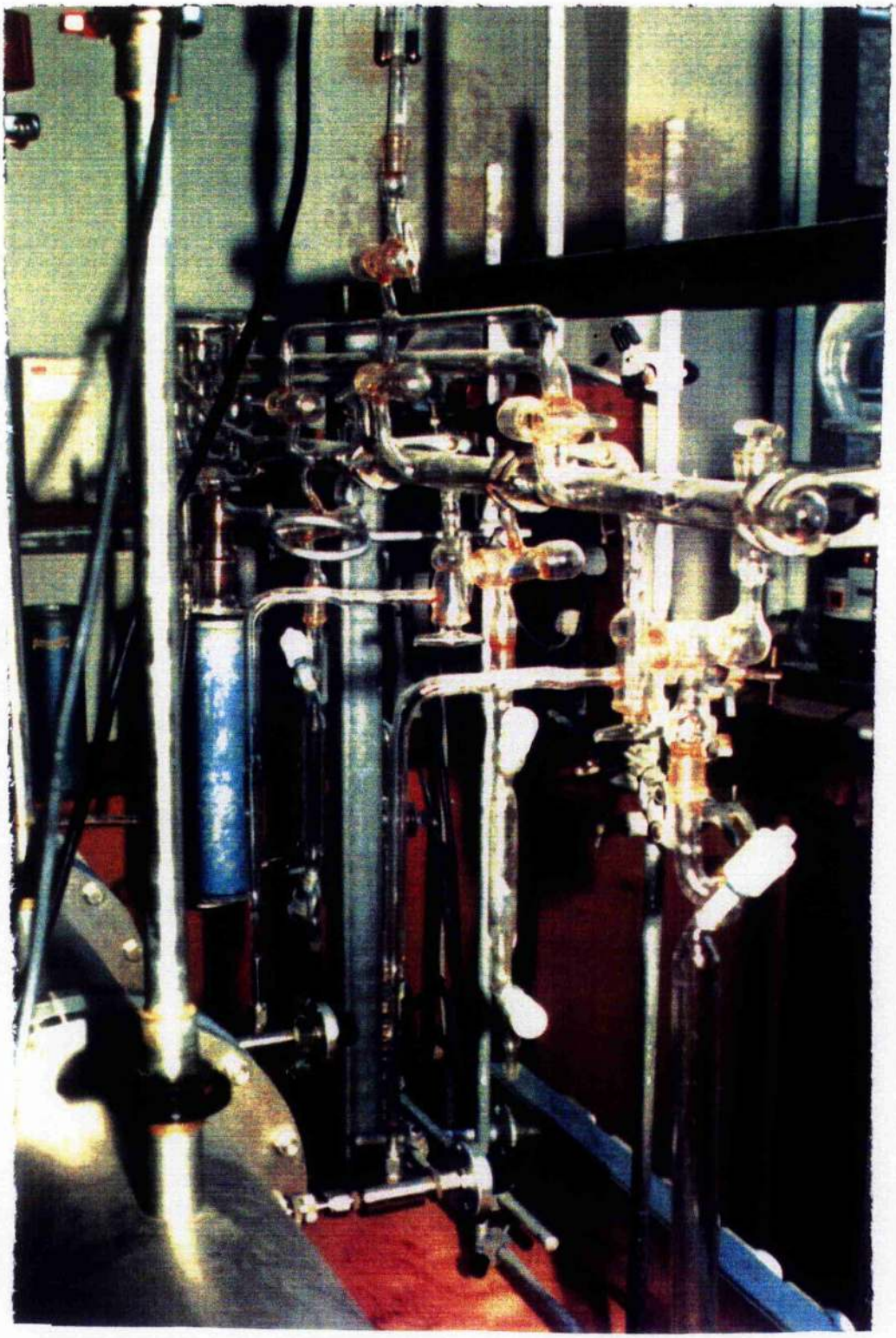
Appendix.

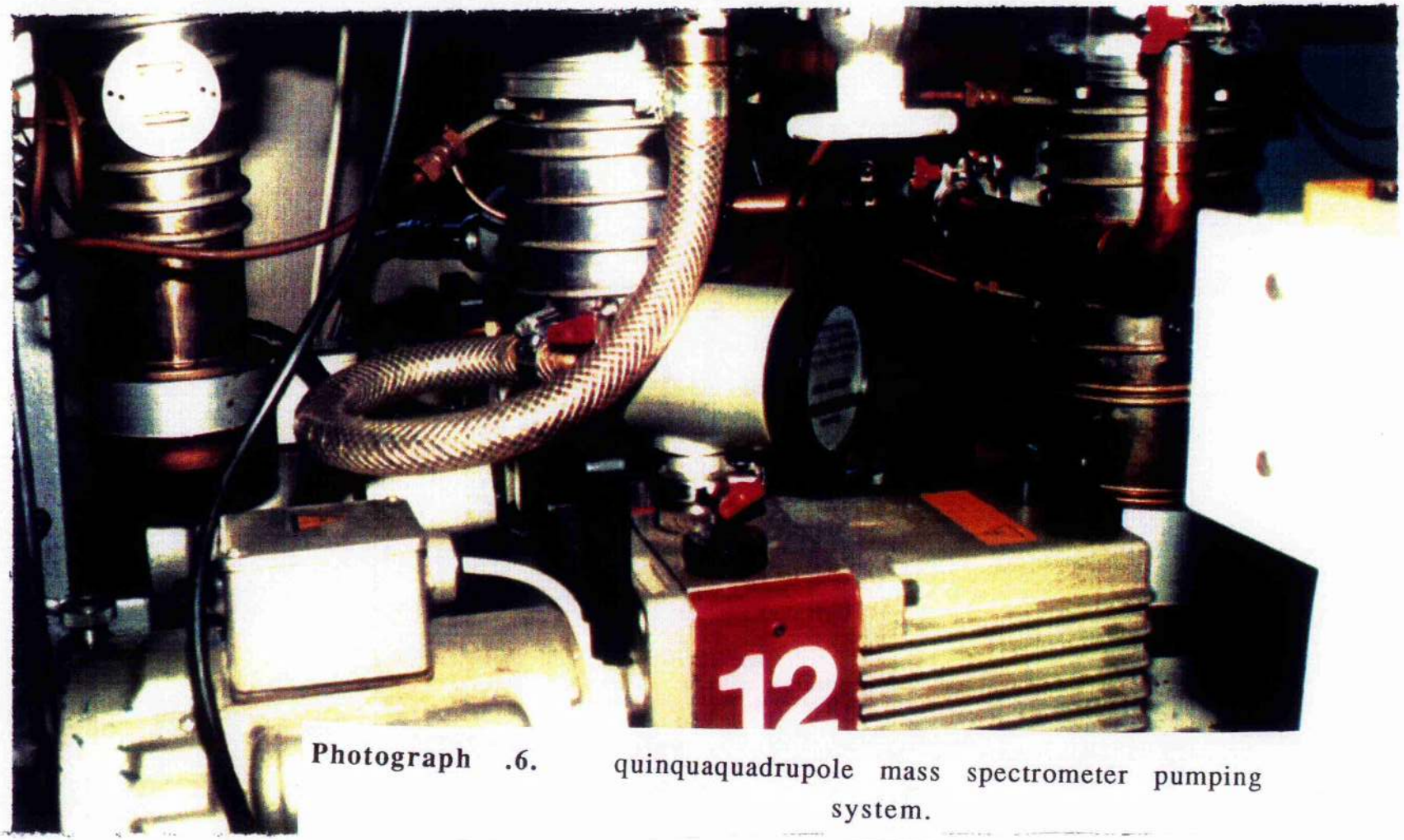
Photographs of the quinquaquadrupole mass spectrometer.



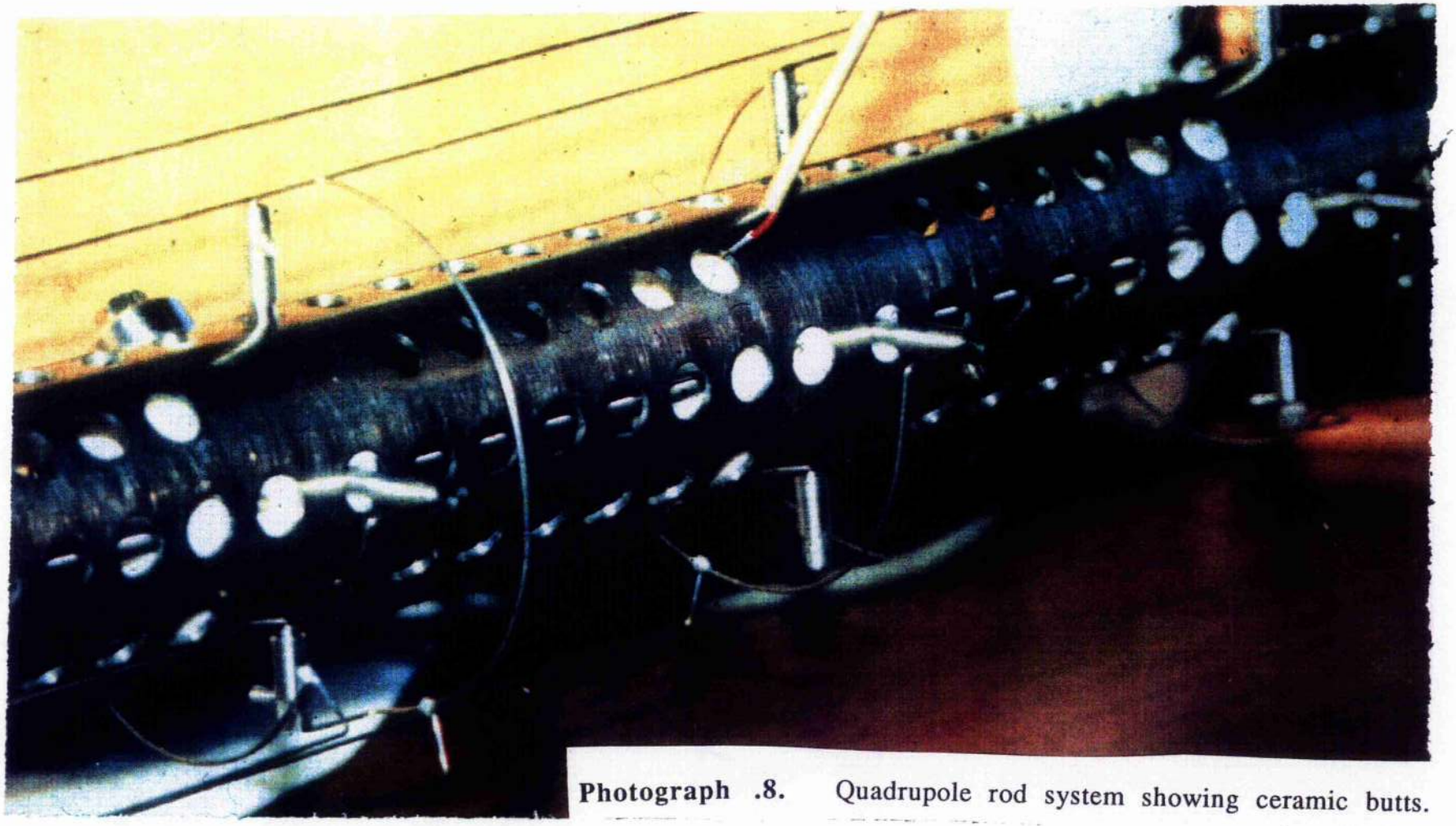
Photograph .4. Typical spectrum from the quinquaquadrupole mass spectrometer.



Photograph .5. Vacuum line to the quinquaquadrupole.



Photograph .6. quinquaquadrupole mass spectrometer pumping system.



Photograph .8. Quadrupole rod system showing ceramic butts.